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## SOIL SCIENCE

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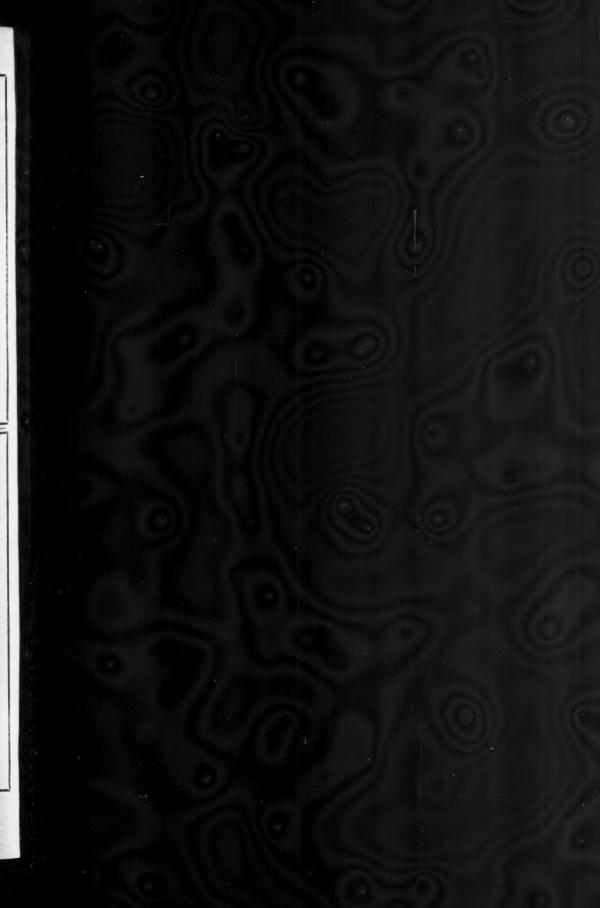
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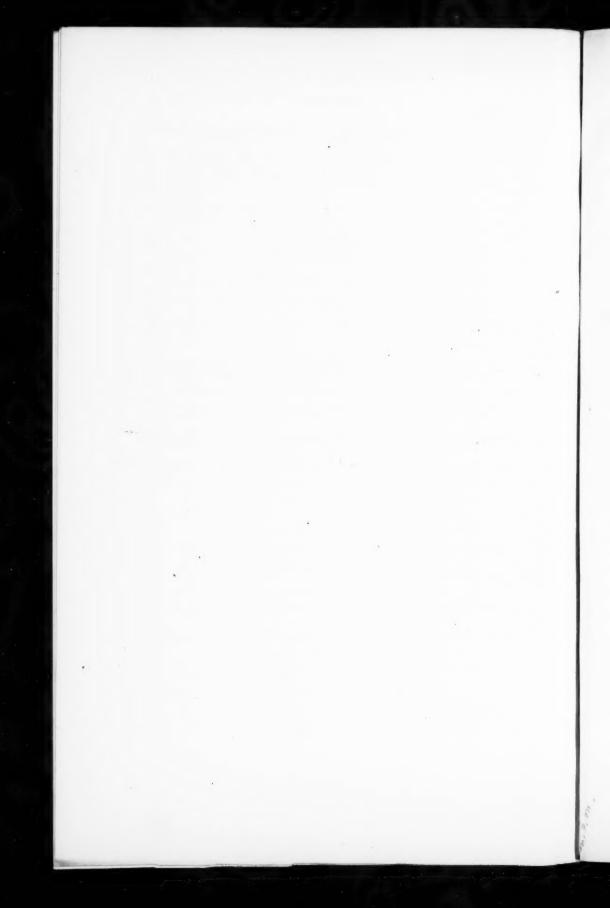
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### A PROPOSED METHOD FOR THE ESTIMATION OF TOTAL CALCIUM IN SOILS AND THE SIGNIFICANCE OF THIS ELEMENT IN SOIL FERTILITY<sup>1</sup>

O. M. SHEDD<sup>2</sup>

Kentucky Agricultural Experiment Station

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#### HISTORICAL

The application of lime and limestone to our soils for better crop production has been so beneficial that there is an increasing inquiry as to the probable need of these materials on areas in different sections of our state. The chief reason for their use has been to overcome an apparent acid condition of the soil, which is most easily done by the use of some base, such as caustic, air-slaked or hydrated lime, limestone or dolomite.

Scientific workers are not always in accord as to the factors which cause soil acidity. This is apparent from the fact that the several methods which have been proposed for its estimation do not always agree when applied in practice. It is generally assumed, however, that so-called acidity bears such a close relation to a calcium deficiency that the terms "acidity" and "lime requirement" are practically synonymous.

Very little significance has been attached to the fact that in adding lime or limestone to soils for correcting acidity, an essential element for plant growth is being applied and one which is removed in comparatively large quantities by crops. Hence any material of this nature is commonly classed as a "soil amendment," rather than as a plant-food. The reason of this is, it is assumed that soils generally contain abundant calcium compounds to furnish an ample supply of this element for all crop requirements. As soil-survey work has progressed, however, analyses show that there are certain types of soil in which the small percentage of total calcium found would indicate that there may be a deficiency of this element for permanent fertility. For example, Hopkins (2) from his work in Illinois, concludes that the addition of limestone to those soils which contain less than 3500 pounds of calcium per surface acre of  $6\frac{2}{3}$  inches in depth, or 0.175 per cent, has a positive value for the calcium which it supplies as plant-food, in addition to any value in correcting soil acidity or improving

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the physical condition. Van Slyke (7) states that certain of the essential elements are more extensively used by crops and sooner or later require special attention in the way of increasing the available supply in some soils. These elements, given in the order of probable importance, are nitrogen, phosphorus, potassium and calcium. Among others who practically agree with the foregoing are Voorhees (8), Halligan (1) and Thorne (5). As stated before, however, very little importance has been attached to a possible deficiency of calcium in soils, for the reason mentioned above and from the further assumption, possibly, that, calcium compounds being quite soluble, even a limited supply will always furnish the necessary amount for the immediate needs of a crop.

#### EXPERIMENTAL

In view of the fact that large amounts of limestone are now being used on the soils of our state and the demand is increasing, the writer thought it would be of interest to study the calcium content of our virgin and cultivated soils in order to determine the effect of cultivation on this constituent. This work has been in progress for some time and the data show some interesting results regarding a possible deficiency of this element, in some cases, for normal crop production. This study has embraced both analytical data on soils and pot cultures in the greenhouse, and is still in progress.

The main difficulty that had to be overcome in the work, at first, was in the estimation of calcium. As ordinarily carried on, it readily became apparent that the method at first used, described in this paper as the "regular method," was defective, for the reasons mentioned later, and this necessitated either an improvement of the same or the substitution of another which would be more satisfactory for this determination.

The methods, briefly described, which have been used are as follows:

Regular method. One gram of soil, ground to pass a 100-mesh sieve, was fused with a 5-gm. fusion mixture (10 parts Na<sub>2</sub>CO<sub>3</sub> + 13 parts K<sub>2</sub>CO<sub>3</sub>) for 10 minutes, in a platinum crucible. The melt was dissolved in distilled water, HCl added, the solution evaporated to dryness and the SiO2 dehydrated by powdering the residue and drying on the water-bath. After dehydration, HCl and H2O were added and the SiO2 filtered and washed. The ammonia precipitation was then made in a faintly ammoniacal hot solution and the precipitate filtered and washed once or twice. It was then dissolved in HCl, reprecipitated in the same way and washed with hot water until free of chlorides. The combined filtrates from the ammonia precipitate were then evaporated to low volume, after being made slightly acid with HCl. At this point, bromine water was added, followed by a moderate excess of NH4OH to precipitate the manganese. After evaporation of excess of NH4OH, the solution was slightly acidified with C2H4O2, the precipitate filtered and washed, only one precipitation of the manganese being made. The filtrate was heated on the bath, a slight excess of NH4OH added and CaC2O4 precipitated with hot, saturated solution of (NH4)2C2O4 and, after standing over night, was filtered, washed a few times, dissolved in HCl and reprecipitated in the same manner.

Modified regular method. The same procedure was used as with the regular method except 2 cc. of 10 per cent FeCl<sub>3</sub> solution was added before the ammonia precipitation was made. The first precipitation of the  $CaC_2O_4$  was made in a faintly ammoniacal solution but the reprecipitation was in weak oxalic acid solution.

Sodium peroxide method. One or two grams of 100-mesh soil were fused with 8 gm. Na<sub>2</sub>O<sub>3</sub> in an iron crucible. The melt was dissolved in water, acidified with HCl, evaporated and SiO<sub>2</sub> dehydrated. The residue was taken up with HCl and H<sub>2</sub>O, filtered and washed until free of chlorides. To the filtrate and washings, in a volume of about 150 cc., was added 0.5 gm. (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, the whole heated to boiling and NH<sub>4</sub>OH added in excess. After boiling for about 5 minutes, the precipitate was filtered and washed with hot water until practically free of chlorides. The filtrate and washings were then acidified with HCl, evaporated to about 100 cc. 1 or 2 cc. of 6 per cent FeCl<sub>3</sub> solution and 0.5 gm. (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>3</sub> added, heated and ammonia precipitation made as before. The filtrate, in a volume of 150 cc., was heated on the bath and hot, saturated (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub> solution added to precipitate the CaC<sub>2</sub>O<sub>4</sub> and allowed to stand over night. The CaC<sub>2</sub>O<sub>4</sub> was filtered, washed a few times, dissolved in HCl and reprecipitated in the same manner.

McCrudden method. After making the fusion as in the "regular method," dehydrating and filtering the SiO<sub>2</sub>, the calcium in the filtrate was determined by the procedure employed by McCrudden (3, 4) for determining calcium in feces, urine, etc. It was thought that this would not give reliable results with soils and for this reason only a few determinations were

made by it.

Preliminary proposed method. The same procedure was followed as in the proposed method to be described later, except the ignition of the CaC<sub>2</sub>O<sub>4</sub> and the treatment to remove manganese was omitted. This method was used at the beginning of the work and, unfortunately, no blanks were run, as the importance of these was not then appreciated.

Proposed method. The fusion of the soil and dehydration of SiO2 was made in the same manner as in the "regular method." The filtrate and washings from the SiO2 should preferably not exceed 100 cc. Concentrated NH4OH was carefully added until the solution was just alkaline to litmus, followed by HCl until the litmus paper was just acid. The precipitate at this point in all cases was not entirely dissolved but rather resembled a colloidal ferric hydroxide solution. It was not thought necessary or even desirable to add HCl until the solution was perfectly clear. The solution was then heated to boiling and 1 to 2 gm. of dry powdered (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub> cautiously added and the heating continued for 2 to 3 minutes. At this point the litmus paper was frequently blue, in which case HCl was added carefully until it was faintly but distinctly acid, the container put on the steam bath for a few hours, and allowed to stand over night at room temperature. The precipitate was filtered until clear, the container carefully washed twice with water, which was poured on the precipitate, and the latter was ignited to convert the calcium oxalate into oxide or carbonate. It was then transferred to the same precipitating container, dissolved in hot dilute HCl, diluted with a small amount of water and heated, after which the manganese was precipitated by the addition of bromine water and a moderate excess of NH4OH. The heating was continued until only a slight excess of NH4OH remained, after which the solution was made slightly acid with C2H4O2, filtered and the filter washed. This was done to remove manganese which was often present. The filtrate was made faintly alkaline with NH4OH and then faintly acid with HCl, boiled and about 0.5 gm. (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, depending on the amount of calcium present, was added as before, the heating continued for 2 to 3 minutes and the same procedure followed as in the first precipitation.

By this method it is possible for one person to average six determinations a day after the work is begun by working on four sets, each comprising six samples, at the same time. If found more convenient, the time allowed for the precipitation of the CaC<sub>2</sub>O<sub>4</sub> may be shortened, as a few minutes' boiling and then allowing to stand for five or six hours on the steam bath will cause complete precipitation. However, it is preferable that the solution be cooled before the filtration is made.

In all methods, it is essential that blanks be run in the same manner as the determinations, the same amounts of chemicals and of water being used, for it has been found here that distilled water prepared from hard water, in the ordinary laboratory still, may contain calcium.

The results obtained both volumetrically and gravimetrically on several soils during the earlier work by these different methods are given in table 1.

TABLE 1

Percentage of total calcium (Ca) in soils found by different methods

SOIL NUMBER	MCCRUD- DEN SODIUM	SODIUM PEROXIDE		REGI	REGULAR		PRELIMI- NARY PROPOSED	PROPOSED
	Vol.	Vol.	Grav.	Vol.	Grav.	Grav.	Vol.	Grav.
	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent
56447	0.212*	0.085	0.200	0.182	0.236	0.129	0.232*	0.186
56447								0.172
56449	0.297*	0.371	0.472	0.373	0.500	0.400	0.444*	0.436
56449								0.429
9768	0.551*	0.615	0.815	0.773	0.879	0.643	0.656*	0.772
9768								0.765
9771	0.127*	0.117	0.307		0.279	0.250	0.211*	0.214
9771								0.207
56485	0.148*	0.386	0.772	0.896	0.707		0.656*	0.572
56487	0.106*	0.197	0.307	0.324	0.329		0.232*	0.279
56457				0.356*	0.457		0.245*	0.236
56459				0.335*	0.400		0.249*	0.293
56517				0.292*	0.386		0.215*	0.272
56519				0.314*	0.357		0.232*	0.250
56521				0.377*	0.443		0.249*	0.229
56523				0.377*	0.393		0.287*	0.257
25662		0.163		0.159	0.372			0.200
25662								0.193
25663		0.108		0.102	0.257			0.143
56493		0.333		0.331	0.550			0.400
56493								0.336
56495		0.201		0.133	0.314			0.207
56513		0.480		0.445	0.672			0.529
56515		0.166		0.138	0.293			0.179

<sup>\*</sup>Determination made on 0.5-gm. aliquots from the same fusion. These particular determinations were made at the beginning when the importance of carrying on blanks in the same manner was partly overlooked. No blanks were run in the McCrudden and preliminary proposed methods but those obtained in the proposed method have been deducted in the preliminary. The McCrudden figures are for the above reason too high but for all other determinations given in this work, the proper blanks have been deducted and unless otherwise stated, were made gravimetrically.

It was apparent at the beginning of the work that the precipitates of CaC<sub>2</sub>O<sub>4</sub> obtained by the regular method were not pure, because the CaO, after ignition, was frequently colored and when it was dissolved in HCl and the solution made faintly alkaline with NH<sub>4</sub>OH, a precipitate was almost invariably obtained.

The amount of this precipitate, however, varied in different cases, and upon examination it was found to consist mainly of alumina, sometimes with very small amounts of iron, phosphorus and manganese compounds present. This fact has frequently been verified by filtering the precipitates, washing and making a third precipitation of the CaC<sub>2</sub>O<sub>4</sub>, in which case lower results have always been obtained, especially in those samples which showed perceptible amounts of impurities. Of course, the presence of these impurities causes a plus error but, on the other hand, if calcium is occluded in the ammonia precipitate, which frequently occurs, a compensating minus error is introduced. These errors may or may not balance each other.

The chief source of error in the regular method is due to the hydrolyzation of phosphates in the ammonia precipitate, or to the hydroxide passing through the filter in a colloidal condition on washing with hot water for the removal of the chlorides. Probably this could be largely obviated by the substitution of some salt solution for the water or by not washing entirely free of chlorides, when the ammonia precipitate is not to be weighed. No attempt has been made along these lines in this work, as it was the writer's desire to demonstrate that the regular procedure, as sometimes prescribed for the separation of calcium in soil analysis (9), does not give accurate results. The factor of preventing hydrolyzation in the washing of precipitates containing mixtures of iron and aluminum phosphates and hydrates has been recognized, however, and the use of a salt wash is sometimes prescribed (6).

It is often recommended that a small amount of ferric chloride be added to the solution when the ammonia precipitation is made, in order to obviate the above difficulty, inasmuch as it makes the precipitate more basic in character, especially where aluminium phosphate is involved, as is the case in soils. This has been done in this work and while it undoubtedly is of value in some instances, still it does not always prevent the difficulty, as will be shown later. It might be mentioned here that in no case wherever tested has the CaO obtained by the proposed method ever shown any impurities of this kind that could be recognized by dissolving the same in HCl and neutralizing with NH<sub>4</sub>OH, and this is further verified by the fact that the entire amount was recovered in the third precipitation.

The gravimetric results obtained by the regular method, with and without the addition of FeCl<sub>3</sub> and subsequently making a third precipitation as above described, are given in table 2. The results obtained from the same samples,

by the proposed method, are included for comparison.

It will be seen from an examination of table 2 that the CaO obtained by the regular method, without the addition of FeCl<sub>3</sub>, generally contained impurities, as was shown by the third precipitation. After the addition of FeCl<sub>3</sub>, the results, as a rule, were much lower, yet the CaO precipitates were not usually pure, as will be seen in the same table. At the same time, however, the results obtained by a third precipitation agree more closely in several instances with those of the proposed method but are still not altogether satisfactory. The

TABLE 2 .

Percentage of calcium (Ca); the regular method, with and without the addition of FeCl<sub>3</sub>, vs. the proposed method

SOIL NUMBER	NO FeCls ADDED	FeCls ADDED	THIRD PRECIPITATION	PDOPOSED METROD
	per cent	per cent	per cent	per ceni
14604	1.415	1.393		1.250
14604		1.265	1	1.293
14604		0.807(a)	0.750(b)	
14604		0.929(c)		
14604		0.886(c)		
14607	0.607(a)		0.429(b)	0.557
14607				0.636
17483	0.536	0.372(a)	0.372(b)	0.407
17483				0.429
25004	0.543	0.314(a)	0.179(b)	0.243
25004				0.200
25549		0.136(a)	0.100(b)	0.107
25549		0.207(c)		0.143
25662	0.372	0.179(a)	0.129(b)	0.200
25662				0.193
36263	0.400	0.079(a)	0.064(b)	0.057
36263		()		0.071
36264	0.329(a)		0.164(b)	0.057
36264	0.025(4)	0.114(a)	0.057(b)	0.036
36264		0.000()	0.00.(0)	0.029
36552	0.372	0.236(a)	0.107(b)	0.093
36552	0.072	0.200(11)	0.10.(0)	0.057
36552				0.036
56463	0.050(a)		0.021(b)	0.136
56463	0.107(a)		0.043(d)	0.079
56463	0.079(a)		0.036(d)	0.179
56463	0.017(a)	0.093(a)	0.100(b)	0.071
56463		0.064(a)	0.043(d)	0.071
56463		0.057(a)	0.014(d)	
36793	0.264(a)	0.007(a)	0.079(b)	0.107
36793	0.201(a)		0.012(0)	0.100
36796		0.457		0.150
36796		0.107(a)	0.121(b)	0.150
56493	0.550	0.372(a)	0.350(b)	0.400
56493	0.550	0.372(a)	0.550(5)	0.336
56494	0.350(a)		0.207(b)	0.214
56494	0.330(a)		0.207(0)	0.172
56496	0.307(a)		0.200(b)	0.172
56496	0.307(a)		0.200(0)	0.104
56455	0.400	0.214(a)	0.143(b)	0.200
56455	0,400	U.214(d)	0.145(b)	0.186
56477	0.350	0.071(a)	0.043(b)	0.114
56477	0.330	0.0/1(a)	U.043(D)	0.100
30411				0.100

TABLE 2-Continued

SOIL NUMBER	NO FeCla ADDED	FeCls ADDED	THIRD PRECIPITATION	PROPOSED METHOI
	per cent	per cent	per cent	per cent
56506	0.172(a)		0.093(b)	0.043
56506				0.064
56508	0.107(a)		0.100(b)	0.036
56508		0.079(a)	0.043(b)	0.029
56510	0.207(a)		0.136(b)	0.057
56512	0.107(a)		0.064(b)	0.064
56512				0.029
56514	0.414(a)		0.272(b)	0.236
56514				0.293
56458	0.414(a)	•	0.279(b)	0.214
56458	0.164(a)		0.172(b)	0.222
56458		0.186(a)	0.193(b)	
56460	0.307(a)		0.207(b)	0.143
56460	0.086(a)		0.064(b)	0.150
56460	0.071(a)		0.043(d)	
56460	0.121(a)		0.050(d)	
56460		0.093(a)	0.071(b)	
56460		0.107(a)	0.036(d)	
56460		0.121(a)	0.050(d)	
56473	0.129(a)		0.100(b)	0.243
56473		0.214(a)	0.179(b)	
56497	0.493	0.200(a)	0.200(b)	0.222
56497				0.243

(a) See (b).

(c) Modified regular method used.

low results can be accounted for only as due to the occlusion of calcium in the ammonia precipitates, while the high ones are undoubtedly caused by impurities.

It has been mentioned that calcium has been found to be occluded in the ammonia precipitate and that such was often the case was proved by an examination made of some samples selected at random that had been used in the work. The calcium was determined by the modified regular method and the ammonia precipitate was dissolved in HCl and the calcium in the same was determined by the proposed method, with the results given in table 3.

As the three methods which were mostly used in the work, namely, the regular, modified regular and proposed, gave such discordant figures on many of the soils, it was thought that it might prove of interest to compare them on a synthetic soil mixture which was comparatively high in calcium, phosphorus and aluminium. Accordingly, a sufficient quantity of a mixture of C.P.

<sup>(</sup>b) The CaO obtained in (a) was dissolved in HCl, made slightly alkaline with NH<sub>4</sub>OH and the precipitate, if any was obtained, was filtered, washed and the third precipitation of CaC<sub>2</sub>O<sub>4</sub> was made in the filtrate in a faintly ammoniacal solution as before.

<sup>(</sup>d) The CaO obtained in (a) was treated as in (b) except the third precipitation of CaC<sub>2</sub>O<sub>4</sub> was made in faint oxalic acid solution.

chemicals in the required amounts was prepared to represent a soil having the composition given in table 4, in 100 parts, the lacking 71.07 parts being supposed to represent SiO<sub>2</sub>, moisture and organic matter. In other words, the 10 parts of SiO<sub>2</sub> used represent only part of that required to make up the supposed soil.

TABLE 3

Percentage of calcium (Ca) occluded in ammonia precipitate in the modified regular method

SOIL NUMBER	MODIFIED REGULAR METHOD	CALCIUM IN AMMONIA PRECIPITATE	TOTAL OBTAINED	PROPOSED METHOD
	per cent	per cent	per cent	per cent
56447	0.129	0.079	0.208	0.186
56447				0.172
56449	0.400	0.057	0.457	0.436
56449				0.429
9768	0.643	0.114	0.757	0.772
9768				0.765
9771	0.250	0.021	0.271	0.214
9771				0.207
14604	0.429	0.529(a)	1.058	1.250
14604		0.100(b)		1.293

(a) and (b), no FeCl<sub>3</sub> was added to (a) or the first ammonia precipitation, but to the resulting filtrate was added 2 cc. of 10 per cent FeCl<sub>3</sub> solution and the second or (b) was then made.

TABLE 4
Composition of synthetic soil mixture

CONSTITUENT	DERIVED FROM
10.00 per cent SiO <sub>2</sub>	0.1000 gm. silica
4.00 per cent Fe <sub>2</sub> O <sub>3</sub>	0.0524 gm. iron oxide, hydrated
10.00 per cent Al <sub>2</sub> O <sub>3</sub> *	0.1039 gm. aluminum oxide, hydrated
1.50 per cent P2O5	0.0258 gm. aluminum phosphate
0.50 per cent MgO	0.0050 gm. magnesia
1.75 per cent CaO	0.0312 gm. calcium carbonate
0.36 per cent SO <sub>8</sub>	0.0101 gm. manganese sulfate
0.32 per cent MnO	0.0101 gm. manganese sulfate
0.50 per cent TiO2	0.0050 gm. titanium oxide
28.93	0.3334 gm.

<sup>\*</sup> Derived from the oxide and phosphate.

The required amount of the above mixture, or 2.0004 gm. representing 6 gm. of soil, was fused with 5 gm. of the double carbonates as in the regular method. Another equal portion, omitting the CaCO<sub>3</sub>, was fused in the same manner for the blanks. The amount of SiO<sub>2</sub> added was, of course, much less than that present in a soil but as this made a thorough fusion more possible and at any rate the SiO<sub>2</sub> is eliminated at the beginning, the above quantity was assumed to exceed largely any that might possibly exist in solution after

the dehydration of SiO<sub>2</sub> was made. The quantity of SiO<sub>2</sub> present in the above fusion was therefore about 75 per cent of the amount in 1 gm. of average soil. No sodium or potassium compounds were added, as the fusion mixture supplied these elements. After the fusions were made and the SiO<sub>2</sub> was eliminated the solutions were made to volume and aliquots corresponding to 1 gm. of soil were used for the calcium determinations, by the different methods. In the regular and modified regular methods, FeCl<sub>3</sub> was added to one aliquot and omitted in the other. The ammonia precipitates were also examined for calcium as in table 3. The results are given in table 5.

The results obtained on the synthetic mixture by all the methods agree very well with the amount of calcium present, and much better than those obtained when the same methods are applied to soils. This corroborates the writer's previous experience, that a synthetic soil solution does not always behave in the same manner as the soil it is supposed to represent. An examination of table 5 shows that the first two methods gave slightly low results

TABLE 5
Occlusion of calcium in ammonia precipitates in regular and modified regular methods

	CaO by METHOD	CaO in ammonia precipitate	TOTAL CaO
	per cent	per cens	per cent
Regular method, no FeCl <sub>3</sub> added	1.67	0.05	1.72
Regular method, FeCl <sub>3</sub> added	1.70	None	1.70
Modified regular method, no FeCl3 added	1.68	0.06	1.74
Modified regular method, FeCl <sub>2</sub> added	1.71	0.01	1.72
Proposed method	1.79		
Proposed method	1.85		
Known content of CaO			1.75

while the proposed method averages a trifle high. In the work on soils, however, the regular method has generally given high results, compared with the proposed method, while the modified method shows both high and low. A tendency also exists here for calcium to be occluded in the ammonia precipitates, which is largely prevented by the addition of FeCl<sub>3</sub>, but this is not so noticeable as it was in the soils.

During this investigation, only a part of which is included in this paper, a large number of soils have been tested comprising samples taken from nearly every county in the state. In many cases the amount of total calcium found was surprisingly low; in fact the lack of this element in several soils was as noticeable as was their deficiency in phosphorus or nitrogen. Taking into account the amounts of these three elements present, two of which, however, are not reported here, and the quantities of the same removed by crops, all are probably deficient in many of the soils. On the other hand, the potassium content of the most of these soils is relatively high and compares favorably with our best in this respect. Some of the results obtained are given in table 6 and in cases where duplicates were made these are included.

TABLE 6

Percentage of total calcium (Ca) in soils found by regular, modified regular and proposed methods

	VIRGIN	SURFACE 0 TO	6 INCHES	CULTIVATED SURFACE 0 TO 6 INCHES			
SOIL NUMBER	Regular	Modified regular	Proposed	Regular	Modified regular	Proposed	
	per cent	per cent	per cent	per cent	per cent	per cent	
56447,9	0.500	0.400	0.436	0.236	0.129	0.186	
56447, 9			0.429			0.172	
36552, 91	0.372		0.093			0.071	
36552			0.057				
36552			0.036				
56467, 17505	0.615		0.314		0.107	0.007	
56467, 17505			0.293			0.036	
36538, 9	0.550		0.472	0.336		0.279	
56469, 71	0.464		0.279	0.279		0.107	
56481, 3	0.786		0.407	0.486		0.186	
56481, 3	0.100		0.386	0.100		0.186	
56485, 7	0.707		0.572	0.329	,	0.279	
9768, 9	0.879	0.643	0.772	0.027		1.458	
9768, 9	0.07	0.010	0.765			1.500	
56497, 9	0.615		0.350	0.493		0.222	
56497	0.010		0.550	0.493		0.243	
56517, 19	0.386		0.272	0.357		0.250	
56477, 9	0.350		0.114	0.500		0.214	
56477	0.550		0.100	0.500		0.214	
36242, 63	0.400		0.057	0.436		0.172	
63	0.400		0.071	0.400		0.112	
56457, 9	0.400		0.293	0.457		0.236	
56513, 15	0.672		0.529	0.293		0.179	
56509, 11	0.243	ĺ	0.150	0.186		0.129	
56493, 5 .	0.550		0.400	0.314		0.207	
56493	0.550		0.336	0.314		0.201	
56505, 7	0.286		0.330	0.229		0.114	
56505, 7	0.200		0.150	0.229		0.057	
36792, 6	0.472		0.179	0.457		0.150	
36792	0.412		0.179	0.437		0.150	
36919, 20			0.079			0.150	
50644, 6			0.079			0.037	
50672, 51362			0.293			0.107	
25771, 2			0.407			0.121	
25787			0.407		0.143	0.086	
25549						0.107	
25549					0.207	0.107	
25814					0.170	0.143	
36819					0.179	0.100	
25828					0.100	0.107	
14976					0.150	0.130	
14976					0.064	0.021	
149/0					0.021	0.030	

TABLE 6-Continued

	VIRGIN	SURFACE 0 TO	S INCHES	CULTIVATI	D SURFACE 0 T	o 6 inches
SOIL NUMBER	Regular	Modified regular	Proposed	Regular	Modified regular	Propose
	per cent	per cent	per cent	per cent	per cent	per cen
17899					0.143	0.114
17341					0.129	0.114
36132					0.136	0.114
17122					0.143	0.157
36507				0.157		0.186
17517						0.029
17517						0.093
17517						0.079
25007						0.02
25007						0.050
25999						0.050
25999						0.07
50904						0.056
50904	-					0.093
25281						0.029
25281						0.09
25281						0.079
25666			1			0.043
25666	- 4					0.05
50787						0.029
50787						0.079
25262					7,1	0.050
25262						0.093
36452						0.09
17901						0.08
25016						0.08
17367						0.10
36493						0.05
36578						0.03

Several virgin soils and the corresponding cultivated samples were used in this investigation in order to determine the loss of calcium due to cultivation. These results, also, are included in table 6.

#### GENERAL DISCUSSION

The proposed method has given more reliable results in this investigation and has several advantages over the regular procedure. It is more rapid, the calcium precipitates are purer and less difficulty in obtaining duplicates is encountered. It has a further advantage in that the handling of the ammonia precipitate, which is always more or less troublesome and which introduces errors in separations of this character, is avoided.

In an ordinary clay analysis, where small amounts of calcium and of other constituents are to be determined, the ammonia precipitate is difficult to

handle and this is further complicated in a soil because much larger amounts of phosphorus, iron, calcium, manganese and other elements are often present. The chief difficulties in the regular procedure have been the hydrolyzation of ferric or aluminium phosphate in the ammonia precipitate and its passing through the filter in a colloidal form on washing with hot water and the occlusion of calcium, probably in the form of phosphate. It was not found possible in all cases to prevent this by the addition of ferric chloride, as is often recommended, but the substitution of a salt solution, such as ammonium nitrate, instead of hot water, might have been very beneficial. This was not tried, for the reason previously stated, but even if it had been, it could only have prevented hydrolyzation or the formation of a colloidal solution, while the error caused by the occlusion of calcium in the ammonia precipitate would still have to be overcome, especially in those soils which had a large content of calcium phosphate. It should be borne in mind that any method for the estimation of total calcium in soils has its limitations when applied to samples that are comparatively low in this element, for a variation of one-tenth of a milligram in the weight of CaO obtained on a one-gram sample is equivalent to 0.007 per cent of the element. Consequently a variation of a few tenths of a milligram in duplicating, which is probably the best that can be expected on such samples, in work of this character, amounts to considerable on soils which contain only a few hundredths of 1 per cent of this element. Disagreement of duplicates when working on soils of this character cannot be attributed altogether either to the method or individual but, even if such duplicates do not agree closely, they undoubtedly show that the soil is low in this constituent.

From an examination of the foregoing tables, it will be observed that some of our cultivated soils are very low in calcium and frequently this holds true for the corresponding virgin soils. In fact, from other work done on these and similar soils but not reported here, their calcium deficiency assumes equal importance with their low phosphorus and even low nitrogen content. An application of one ton of limestone or of calcium phosphate per acre to such soils frequently supplies more calcium than is already present. In such cases there can hardly be any doubt that the increased plant growth following applications of these materials, or even of some commercial fertilizers, is due, at least in part, to the plant-food calcium which these materials supply, in addition to other good results which they may accomplish.

#### SUMMARY

1. The procedure which is often used and has been adopted by the Association of Official Agricultural Chemists for the determination of calcium in a soil solution does not give accurate results.

2. The chief difficulties encountered in its use have been due to the passage through the filter of iron and aluminium compounds either from hydrolyzation of ferric and aluminium phosphates in the ammonia precipitate or in a colloidal

condition caused by washing with hot water, and to the occlusion of calcium, probably as the phosphate, in this precipitate.

- Attempts to prevent these errors by the addition of ferric chloride have not been successful.
- 4. Other modifications of the above procedure and substitution of other methods have not been altogether satisfactory for this determination when the process involved separation of the ammonia precipitate previous to the estimation of the calcium.
- 5. A proposed method which eliminates the chief sources of error of the regular procedure has been found to give more concordant results and is more rapid.
- 6. When some of the methods used in this work were tried on a synthetic soil solution a better agreement was obtained than when the same were applied to soils. This verifies the author's previous experiences that a synthetic solution does not always act in the same manner as a solution of the soil which it is supposed to represent.
- 7. The total calcium content of a large number of Kentucky soils, both virgin and cultivated, has been determined, and it appears in nearly every instance that cultivation has caused a considerable loss of this element.
- 8. From an investigation of which this work is only a part and which has included several hundred samples taken from nearly all the counties in this state, it has been found that the best types of soil contained the highest content of calcium and the poorest had the lowest.
- Many samples have been found to be so low in calcium that their deficiency in this constituent requires consideration as well as their low phosphorus and nitrogen supply.
- 10. The application of a ton of limestone or of rock phosphate per acre to such soils frequently adds more calcium than is already present.
- 11. There is no doubt that, in such cases, these materials, or even moderate applications of some commercial fertilizers, are beneficial because of the plant-food calcium they supply, in addition to other good effects they may accomplish.

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#### THE USE OF CARBON BISULFIDE AGAINST THE WHITE GRUBI

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#### INTRODUCTION

The control of soil-infesting insects has always been an exceedingly vexatious problem for the economic entomologist. Their subterranean feeding habit renders them immune to the ordinary methods of control by stomach poisons or contact insecticides, while in many cases the 2- or 3-year life cycle adds another complication to an already complex problem. The usual recommendations for the control of such pests are crop rotation and fall plowing.3 These methods, while quite applicable to crops which mature in one growing season, are impracticable when infestation occurs on plants or crops of a more permanent nature. In New Jersey the greatest recent injury has occurred in lawns, golf-greens and strawberry beds. In lawns and golf-greens the nature of the injury is such that the roots of the grass are eaten off just below the surface of the ground. In strawberry beds the injury is done when the plants are set out in land which was previously in sod; in this case the roots of the plants are cut off below the crown, resulting in extreme cases in the loss of the entire bed. For this injury the common white grubs, larvae of Lachnosterna beetles, are responsible. In order to effect a feasible control of these insects when present in such locations, some method must be devised which will exterminate the insect, and at the same time not injure the plant it is infesting. The method chosen for this purpose was soil fumigation with carbon bisulfide. The problem to be solved was to determine whether a dosage could be found which would be fatal to the grub, and at the same time not injure the plant. The problem was divided into three parts, the determination of the maximum dosage non-injurious to the plant, the determination of the minimum dosage lethal to the grub, and the determination of the influence of temperature and moisture conditions upon the effectiveness of the fumigation.

<sup>1</sup> Technical Paper No. 5 of the New Jersey Agricultural Experiment Station, Department of Entomology.

<sup>2</sup> This investigation was suggested by and carried out under the supervision of Dr. Thomas J. Headlee, Professor of Entomology at Rutgers College, to whom I wish to express my indebtedness for aid and encouragement throughout the course of the work.

<sup>3</sup> Since this paper was written sodium cyanide has been successfully used against white grubs by F. A. Kaufman of the Roessler and Hasslacher Chemical Company, by W. H. Goodwin and finally by J. J. Davis of the Riverton Entomological Laboratory.

The material for the studies on the control of the white grub was obtained during the fall of 1915. The grubs were dug from an uncultivated field in sod where they were found at the roots of grass and weeds. The material was preserved alive according to the method given by J. J. Davis (1). Briefly outlined, this method consists of placing a single grub in a small tin ointment box, with moist earth, and carefully sterilized wheat which has been deprived of germinating power by heat. The necessity for killing the wheat and sterilizing it was shown by previous experience, when the wheat kernels germinated inside the boxes, and fungus spores attacked the wheat in other boxes, rendering it unfit for larval food. By this method of preservation, larvae were kept alive and vigorous from October, 1915, to May, 1916.

#### DETERMINATION OF THE MAXIMUM DOSAGE NON-INJURIOUS TO PLANTS

The first phase of the problem, the determination of the maximum dosage non-injurious to plants, was attacked by trying the effect of carbon bisulfide on plants grown in the greenhouse. The flats in which the plants were grown

TABLE 1
Temperature of soil and of air—first maximum dosage experiment

	A	IR .		BLUEGRASS		BLUEGRASS AND CLOVER		
DATE	Maximum	Minimum	Soil dry	Soil medium	Soil wet	Soil dry	Soil medium.	Soil wet
	°F.	°F.	°F.	°F.	°F.	°F.	°F.	°F.
2- 5-16	92	68	64	64	63	71	70	64
2- 7-16	73	651	73	75	72	72	71	70
2- 8-16	651	47	63	63	61	65	64	62
2- 9-16	831	58	67	66	631	70	72	62
2-10-16	83	60	69	70	73	70	73	71
?-11-16	80	58	57	61	611/2	60	60	60
2-12-16	80	57	58	60	61	60	60	61
2-14-16	60	45	50	49	50	49	48	49

were 31 by 15 inches and 6 inches deep. Inasmuch as lawns are chiefly made up of a mixture of Kentucky bluegrass and white clover, six flats were planted: two flats each of bluegrass, of white clover and of a mixture of the two. These flats were prepared for the experiments by enclosing a section having an area of 1 square foot, and a depth of 5 inches (the depth of the greenhouse bench) in a square casing of galvanized iron, which was driven down to the bottom of the bench. Carbon bisulfide (Lehn and Fink, technical) was introduced into each of three flats, one flat each of bluegrass, clover, and a mixture of the two, at the rate of 2 ounces to each section. The dose was introduced by means of a pipette into a hole 3 inches deep placed in the center of the section. Soil and air temperatures are recorded in table 1. Determinations of the actual soil moisture were not made, but it is thought that they were about the same as shown in later experiments on page 23.

A month after the introduction of the carbon bisulfide no apparent injury had been done to any of the plots with the 2-ounce charge of carbon bisulfide, except for the very slight contact kill incidental to the introduction of the material. This experiment demonstrates that under the above conditions, 2 ounces of carbon bisulfide may be used on bluegrass, white clover, or a mixture of the two, without injury to the plants.

As a continuation of the above experiments, six flats of the same dimensions as those used in the preceding experiment, containing timothy, red clover,

TABLE 2
Temperature of soil and of air—second maximum dosage experiment

A	TR	TIM	OTHV	CLO	VER	TIMOTHY A	ND CLOVE
Maximum	Minimum				7 2000		410 020121
°F.	°F.	°F.	°F.	°F.	°F.	°F.	°F.
66	54 {	53 50	53 50	47 51	47 51	54 55	54 54
621/2	50 {	50 49	50 49	46 48	46 48	50 51	50 51
69	50 {	54 51	54 51	49 53	50 53	54 56	54 65
72	46 {	55 54	55 54	54 55	54 55	53 55	54 55
72	48 {	55 54	55 53	52 53	52 53	56 56	55 56
73	47 {	61 60	61 60	59 60	59 60	61 61	61 60
71½	48 {	60 61	60 61	58 59	58 59	60 59	59 59
73	52 {	61	62	60	61	62	62 62
	Maximum  *F.  66  62½  69  72  72  73  71½	°F.     °F.       66     54       62½     50       69     50       72     46       72     48       73     47       71½     48       48     (	Maximum   Minimum   *F.   *F	Maximum   Minimum   *F.   *F	Maximum   Minimum	Maximum   Minimum	Maximum   Minimum   FIMOTHY   CLOVER   TIMOTHY A

and a mixture of the two, were divided into two parts by a board partition. Thus, four plots of each mixture were formed.

The plots of timothy, red clover and the mixture of the two designated as No. 1 received 2 ounces of carbon bisulfide; those designated as No. 2, No. 3 and No. 4 received  $1\frac{1}{2}$  ounces, 1 ounce, and  $\frac{1}{2}$  ounce, respectively. Maximum and minimum temperatures were taken daily except Sundays. Table 2 below gives the soil and air temperatures.

Eleven days after the introduction of the carbon bisulfide an examination of the plots for injury was made. The results are given in table 3.

As conclusions to be drawn from the experiment, at a temperature of 60°F. or below, 1 ounce of carbon bisulfide has no deleterious effect on such plants as timothy and red clover. Amounts in excess of 1 ounce are slightly injurious to clover, but injury to timothy was negligible. In all these experiments on plants, the plants were at the most only 6 weeks or 2 months old, and were vigorously growing. In other words, their rate of metabolism was very high, and they were in a favorable condition for injury to occur from the use of so toxic a material as carbon bisulfide.

The next experiment to determine the lethal dosage for plants duplicated the method used in the first experiment with Kentucky bluegrass and white clover. Plants of the same kind were used, being placed under as nearly

TABLE 3

Effect of carbon disulfide applications—maximum dosage experiments

PLANT	NUMBER OF PLOT	DOSAGE	REMARKS
		ounces	
1	1	2	Slight injury at point of introduction
TP:41	2 3	11/2	Injury less than preceding
Timothy	3	1	No apparent injury
-	4	1/2	No apparent injury
-	1	2	Injury greatest at point of application. Many plants killed
Red clover	2	11/2	Injury less
	2 3	1	No perceptible injury
(	4	$\frac{1}{2}$	No injury
. (	1	2	Few timothy plants killed. All clover dead near hole
Timothy and red clover	2	11/2	Clover suffered more than timothy, which was little injured
	3	1	Scattering injury to clover, none to timothy
	4	1/2	Clover slightly injured. No injury to timothy

similar conditions of soil moisture as possible, but the temperature was not controlled, as this was impracticable under greenhouse conditions. In this experiment the effect of higher dosages with carbon bisulfide was tried. A uniform dose of 5 ounces to the square foot was applied in the same manner as in the preceding experiment. Soil and air temperatures were taken daily and are given in table 4.

The moisture of the soils at the beginning of the experiment was: dry 5.29 per cent, medium 10.73 per cent, wet 21.37 per cent on the bluegrass plots; on the mixed plots it was: dry 6.07 per cent, medium 12.97 per cent, wet 19.56 per cent.

Three weeks after the beginning of the experiment, no injury was apparent to any of the plots except one of bluegrass. This plot received exactly the same treatment as all the other plots, and no reason can be detected for the effect of the carbon bisulfide in this case, if indeed the carbon bisulfide was responsible for the injury. The bluegrass in the plot containing the mixture of bluegrass and white clover was ininjured.

According to these results apparently 5 ounces of carbon bisulfide can be used under the above conditions without injury to a mixture of bluegrass and white clover.

Experiments performed outdoors on a lawn seem to show that a dosage of 5 ounces is injurious to grass. A plot of grass near the greenhouse was selected, and a series of holes made with a dibble. Six rows of four holes each were made, with the holes one foot apart in each row and the rows one foot apart. In the first and fourth rows the holes were 3 inches deep; in the second and

TABLE 4

Temperature of the soil and of the air—first lethal dosage experiment

	Al	TR.		BLUEGRASS			BLUEGRASS AND CLOVER		
DATE	Maximum	Minimum	Soil dry	Soil medium	Soil wet	Soil dry	Soil medium	Soil we	
	°F.	°F.	°F.	°F.	F.	°F.	°F.	°F.	
3-11-16	92	54	63	64	62	63	62	63	
3-12-16	86	60	70	68	71	72	70	70	
3-13-16	75	53	72	73	69	73	70	70	
3-15-16	78	52	73	73	72	73	69	68	
3-16-16	70	41	70	68	66	69	70	67	
3-17-16	83	47	74	72	70	72	70	70	
3-18-16	86	42	69	69	64	70	68	66	
3-20-16	86	51	69	70	69	71	68	67	
3-22-16	93	51	74	72	72	75	71	70	

fifth rows 6 inches deep, and in the third and sixth rows 12 inches deep. A line passed through the center of each row divided the plot into two equal parts, one of which was watered freely, while the other was not watered.

The first three rows, consisting of twelve holes, received a charge of 1 ounce per hole, while the last three rows received a charge of 5 ounces per hole. About 2 weeks after the charge had been placed, the plot was examined, and it was found that while there was no injury to the grass which surrounded the holes in which a 1-ounce charge had been placed, all the grass for a distance of approximately 4 inches from the hole had been killed by the application of 5 ounces. Neither the depth of the hole nor the moisture condition seemed to influence the result, as the killing was quite uniform with a 5-ounce charge. With the facts ascertained previously in hand, it was not deemed necessary to use a greater charge than 5 ounces, as the lethal dose appeared to be somewhere in the neighborhood of 5 ounces or less. The soil temperature at the beginning of the experiment was 63°F. and did not vary greatly during the week next succeeding the application.

#### MINIMUM DOSAGE LETHAL TO THE GRUB

The second phase of the problem, the determination of the minimum dosage lethal to the grub, was attacked by placing the grubs in small wire cylinders, which were buried at varying depths in the soil of the greenhouse flats; the flats in turn were treated with varying doses of carbon bisulfide.

The type of soil used in these experiments was the red shale decomposition product known as Penn loam, a heavy, red, clayey soil, baking readily on drying, and cracking after being puddled. Four flats were used, twelve grubs

TABLE 5
Temperature of soil and of air—second lethal dosage experiment

DATE	A	IR		SOIL	
DALL	Maximum	Minimum	Dry	Medium	Wet
	°F.	°F.	°F.	°F.	°F.
		1	681	70	661
2-9-16	83.5	58	72	67	66
		1	72	70	62
		1	681	681	65
2-10-16	83	60	72	69	$64\frac{1}{2}$
			711/2	69½	64
*+ ,		(	671	65	57
2-11-16	80	58	69	621	56
			69	671/2	58
		ſ	62	59	60
2-12-16	70	58	611	561	57
			62	60	58
2-13-16	80	57	Sunday		
		(	51	50	50
2-14-16	61	42	51	49	48
,			51	47	46

being placed in each flat. The first flat received 1 ounce, the second 0.5 ounce, the third 0.1 ounce, and the fourth, a check, received no treatment. The grubs were placed in cylindrical galvanized iron wire cages 4 inches long and  $1\frac{1}{2}$  inches in diameter. Two grubs, separated from each other by a cotton plug, were placed in each cage, together with wheat grains for food.

The cages were placed in the soil at two distances from the point of injection of the carbon bisulfide, and at two depths from the surface. Two cages were placed at a distance of 12 inches from the point of injection, on opposite sides of the point, one at a depth of 1 inch and the other at 5 inches below the soil surface. Four others were placed 6 inches from the point of injection,

 $90^{\circ}$  apart, so arranged that of each pair of cages  $180^{\circ}$  apart, one cage was 1 inch below the surface, and the other 5 inches below the surface of the soil.

The carbon bisulfide was injected into the soil by means of a pipette, at a distance of 3 inches below the surface.

Soil and air temperatures were recorded daily during the course of the experiment, and are given in table 5.

The conclusions to be drawn from this experiment are that the minimum dose for the white grub lies in the neighborhood of 1 ounce per square foot, at an average temperature of 60° to 65°F., and that deeper-lying forms, provided the depth does not exceed 6 inches, are much more strongly affected than the shallow-lying individuals.

TABLE 6

Effect of carbon bisulfide on white grubs—lethal dosage experiments

DOSE	DISTANCE	DEPTH	NUMBER PLACED	NUMBER DEAD	NUMBER ALIVE	MORTALITY
ounces	inches	inches				per cent
0.1	12	5	2	0	2	0
0.1	12	1	2	0	2	0
0.1	6	5	4	0	4	0
0.1	6	1	4	0	4	0
0.5	12	5	2	2	0	100
0.5	12	1	2	0	2	0
0.5	6	5	4	4	0	100
0.5	6	1	4	2	2	50
1.0	12	5	2	2	0	100
1.0	12	1	2	0	2	0
1.0	6	5	4	4	0	100
1.0	6	1	4	2	2	50

## THE INFLUENCE OF TEMPERATURE UPON THE EFFECTIVENESS OF THE FUMIGATION

A series of experiments was next performed to determine the influence of temperature upon the effectiveness of fumigation. The first step was to determine the amount of carbon bisulfide which, when vaporized in air at a known temperature, would constitute a sublethal dose; in other words, a charge which would almost but not quite kill the grubs exposed to it. This determination was necessary in order to give a starting-point from which to determine whether an increase in temperature with the same dose would result in any increase in the effectiveness of the fumigant.

To determine this sublethal dose, grubs were placed in 2-liter Mason jars, which could be hermetically sealed by means of a rubber ring and a glass cap. Varying amounts of carbon bisulfide were placed in the jars, and at the end of 24 hours the grubs were removed and examined for signs of life. It was found that the fumigant had a stupefying effect in cases where it did

not kill outright, for many grubs which, when first removed from the jars, showed no signs of life were very active 24 hours after removal from the jars containing the fumigant. In this manner it was found that at a temperature of 65°F., 5 drops, or approximately 0.2 cc., of carbon bisulfide in 2000 cc. of air will not kill, while 10 drops in 2000 cc. was fatal to all grubs subjected to it. The experiment was checked through twice in order to make sure of the dosage.

The experiment was then tried on grubs in the soil. The volume of air remaining in a container, when filled as completely as might be with soil, was determined approximately by displacing the air with water. In this way it was determined that the container held about 425 cc. of air in addition to the soil it contained when full. On this basis, fumigation in air-tight containers in chambers in which the temperature could be maintained constant was tried. The necessary temperature was maintained by electric-light bulbs of different filaments and candle-power, contained in the chambers. The temperature was first regulated in the chambers before placing the grubs in the containers, and then the grubs were placed in the soil and the containers sealed. The larvae were allowed to become acclimatized for 24 hours before introducing the carbon bisulfide. One drop of the fumigant to each container was used, corresponding to one drop to each 425 cc. of air. This in turn corresponds closely to the dosage determined before as not fatal to the grub at a temperature of 65°F. A series of temperatures was run, beginning at 65°F. and including 75°F., 85°F., 95°F. and 105°F. The temperature of 105°F. could not be used in a fumigation experiment, as of itself it was sufficient to kill the grubs in 24 hours without the addition of carbon bisulfide.

The results of the experiment were as follows:

At 65° F. one drop of CS2 in 425 cc. of air will not kill.

At 75° F. one drop of CS2 in 425 cc. of air will not kill.

At 85° F. one drop of CS2 in 425 cc. of air will kill.

At 95° F. one drop of CS2 in 425 cc. of air will kill.

At 105° F. the grubs were killed by the heat effect alone.

Thus it is shown that the effectiveness of the fumigation is dependent upon the temperature, being more effective at the higher temperatures. This is in accord with the literature in regard to fumigation against other insect pests.

#### THE INFLUENCE OF MOISTURE UPON THE EFFECTIVENESS OF FUMIGATION

In this series of experiments the effect of soil moisture was investigated, to discover any relationship between soil moisture and effectiveness of fumigation. The soil type used was the same as that in the experiments upon the minimum dosage for the grubs (page 20). Three soil-moisture conditions were used, being determined according to the Official Methods for Soil Analysis, as follows: wet, moisture 24.72 per cent, medium moisture 12.3 per cent,

and dry moisture 4.67 per cent. Three charges of carbon bisulfide were used, 0.1 ounce, 0.5 ounce, and 1 ounce. Twelve flats were used, each 15 by 30 inches and 6 inches deep, all filled with the same type of soil. These were divided into four series of three flats each, on a basis of the dose received. The first series of three flats were treated with the 0.1-ounce charge, the second with the 0.5-ounce charge, and the third with the 1-ounce charge, while the fourth, a check, received no treatment. In each of these series of three flats, one flat contained dry soil, the second medium-moist soil, and the third, wet soil. The grubs were placed in cylinders of the same kind as described under the heading "Minimum dosage lethal to the white grub."

TABLE 7

Temperature of the soil and of the air—moisture experiments, first trial

DATE	A	tr.		SOIL	
DAIL	Maximum	Minimum	Dry	Medium	Wet
4	°F.	°F.	°F.	°F.	°F.
		(	681	70	661
2- 9-16	831	58	72	67	66
		(	72	70	62
		(	681/2	681	65
2-10-16	83	60	72	69	641
		(	711/2	69½	64
		1	671	65	57
2-11-16	80	58	69	621/2	56
		(	69	671	58
		(	62	59	60
2-12-16	70	58	611	561	57
	,		62	60	58
2-13-16	80	57	Sunday		
		1	51	50	50
2-14-16	61	42	51	49	48
			51	47	46

The arrangement of the cages was the same as described under that heading. The carbon bisulfide was injected into the soil by means of a pipette, at a distance of 3 inches below the surface.

Soil and air temperatures were recorded daily during the course of the experiment, and are given in table 7.

The record for the dry plot is presented in table 8.

Table 9 shows the record on the medium-moisture plot.

The record on the wet plot is given in table 10.

The experiments were repeated in order to determine whether any effect could be obtained by trying to keep the carbon bisulfide within the soil by means of a blanket of moisture, which would tend to prevent the rapid diffusion upward through the surface layers of the soil. All conditions for this experiment duplicated as nearly as possible those of the preceding, the soil

TABLE 8

Effect of carbon bisulfide on white grubs in the dry plot—first trial

DOSE	DISTANCE	DEPTH	NUMBER PLACED	NUMBER DEAD	NUMBER ALIVE	MORTALITY
ounces	inches	inches				per cent
0.1	12	5	2	0	2	0
0.1	12	1	2	0	2	0
0.1	6	5	4	0	4	0
0.1	6	1	4	0	4	0
0.5	12	5	2	0	2	0
0.5	12	1	2	. 0	2	0
0.5	6	5	4	0	4	0
0.5	6	1	4	0	4	0
1.0	12	5	2	0	2	0
1.0	12	1	2	0	2	0
1.0	6	5	4	2	2	50
1.0	6	1	4	0	4	0

The average soil temperature in the dry plot, with a dose of 0.1 ounce, was 63.5°F. The average soil temperature in the dry plot, with a dose of 0.5 ounce, was 65.1°F. The average soil temperature in the dry plot, with a dose of 1 ounce, was 65.1°F.

TABLE 9

Effect of carbon bisulfide on white grubs in the medium-moisture plot—first trial

DOSE	DISTANCE	DEPTH	NUMBER PLACED	NUMBER DEAD	NUMBER ALIVE	MORTALITY
ounces	inches	inches				per cent
0.1	12	5	2	0	2	0
0.1	12	1	2	0	2	0
0.1	6	5	4	0	4	0
0.1	6	1	4	0	4	0
0.5	12	5	2	0	2	0
0.5	12	1	2	0	2	0
0.5	6	5	4	0	4	0
0.5	6	1	4	1	3	25
1.0	12	5	2	0	2	0
1.0	12	1	2	0	2	0
1.0	6	5	4	0	4	0
1.0	6	1	4	0	4	0

The average soil temperature in the medium-moisture plot was 62.5°F., with a charge of 0.1 ounce.

In the plot with 0.5 ounce the average soil temperature was 59°F.

In the plot with the 1-ounce charge the average temperature was 63°F.

moisture being the same within a fraction of 1 per cent, the only difference being in the amount of carbon bisulfide which was injected into the flats. These new dosages were 0.5 ounce, 1 ounce, and 1.5 ounce. Immediately after introducing the carbon bisulfide, the soil was blanketed with moisture

TABLE 10

Effect of carbon bisulfide on white grubs in the wet plot—first trial

DOSE	DISTANCE	DEPTH	NUMBER PLACED	NUMBER DEAD	NUMBER ALIVE	MORTALITY
ounces	inches	inches				per cent
0.1	12	5	2	0	2	0
0.1	12	1	2	0	2	0
0.1	6	5	4	0	4	0
0.1	6	1	4	0	4	0
0.5	12	5	2	2	0	100
0.5	12	1	2	0	2	0
0.5	6	5	4	4	0	100
0.5	6	1	4	2	2	50
1.0	12	5	2	2	0	100
1.0	12	1	2	0	2	0
1.0	6	5	4	4	0	100
1.0	6	1	4	2	2	50

The average soil temperature in the plot receiving 0.1 ounce was 63.5°F.

TABLE 11
Temperature of the soil and of the air—moisture experiments, second trial

DATE	A	R	SOIL				
DAIL	Maximum	Minimum	Dry	Medium	Wet		
	°F.	°F.	°F.	°F.	°F.		
		(	79	80	70		
3-11-16	92	54	71	73	70		
		(	72	78	71		
		(	70	77	69		
3-13-16	86	60	68	71	69		
		1	67	69	70		
			66	62	68		
3-14-16	75	53	65	68	64		
			63	62	62		

sprinkled on gently over the surface of all the plots. Air and soil temperatures were recorded daily, and are presented in table 11.

The records on the plots are given in tables 12, 13 and 14.

A dry check was run, receiving no fumigation. All grubs were alive when examined at the end of the experiment.

The average soil temperature in the plot receiving 0.5 ounce was 62°F.

The average soil temperature in the plot receiving 1 ounce was 64°F.

TABLE 12

Effect of carbon bisulfide on white grubs in the dry plot—second trial

DOSE	DISTANCE	DEPTH	NUMBER PLACED	NUMBER DEAD	NUMBER ALIVE	MORTALITY
ounces	inches	inches				per cent
0.5	12	5	2	0	2	0
0.5	12	1	2	0	2	0
0.5	6	5	4	3	1	75
0.5	6	1	4	0	4	0
1.0	12	5	2	0	2	0
1.0	12	1	2	0	2	0
1.0	6	5	4	3	1	75
1.0	6	1	4	0	4	0
1.5	12	5	2	0	2	0
1.5	12	1	2	0	2	0
1.5	6	5	4	3	1	75
1.5	6	1	4	0	4	0

TABLE 13

Effect of carbon bisulfide on white grubs in the medium plot—second trial

DOSE	DISTANCE	DEPTH	NUMBER PLACED	NUMBER DEAD	NUMBER ALIVE	MORTALITY
ounces	inches	inches				per cent
0.5	12	5	2	0	2	0
0.5	12	1	2	0	2	0
0.5	6	5	4	0	4	0
0.5	6	1	4	0	4	0
1.0	12	5	2	1	1	50
1.0	12	1	2	0	2	0
1.0	6	5	4	4	0	100
1.0	6	1	4	0	4	0
1.5	12	5	2	1	1	50
1.5	12	1	2	1	1	50
1.5	6	5	4	4	0	100
1.5	6	1	4	3	1	75

TABLE 14

Effect of carbon bisulfide on white grubs in the wet plot—second trial

DOSE	DISTANCE	DEPTH	NUMBER PLACED	NUMBER DEAD	NUMBER ALIVE	MORTALITY
ounces	inches	inches				per cent
0.5	12	5	2	0	2	0
0.5	12	1	2	0	2	0
0.5	6	5	4	1	3	25
0.5	6	1	4	0	4	0
1.0	12	5	2	1	1	50
1.0	12	1	2	0	2	0
1.0	6	5	4	3	1	75
1.0	6	1	4	1	3	25
1.5	12	5	2	0	2	0
1.5	12	1	2	1	1	50
1.5	6	5	4	4	0	100
1.5	6	1	4	3	1	75

In order to check against the possibility of diffusion of the carbon bisulfide downward through the bottom of the wooden flats used, a determination of the killing effect of carbon bisulfide was made in two galvanized iron pans, each having the same dimensions as the wooden flats used in the experiments. In this experiment two degrees of soil moisture were used, very dry (3.97 per cent moisture) and wet (24.03 per cent moisture). The soil was the same as that used in the other experiments in the wooden flats. The dosage was 1 ounce. Grubs in galvanized wire cages were placed as in the previous experiments. Soil and air temperatures are given in table 15 and the results in table 16.

TABLE 15

Temperature of the soil and of the air—experiment in iron pans

DATE	SOIL MOISTURE	SOIL TEMPERATURE	AIR TEMPERATUR
		°F.	°F.
4-15-16	Wet	80	
	Dry	84	88
4-17-16	Wet	76	
	Dry	80	84

TABLE 16
Effect of the funigation on white grubs

DOSE	DISTANCE	DEPTH	SOIL	NUMBER PLACED	NUMBER DEAD	NUMBER ALIVE	MORTALITY
ounces	inches	inches					per cent
1	12	5	Wet	2	1	1	50
1	12	1	Wet	2	0	2	0
1	6	5	Wet	4	4	0	100
1	6	1	Wet	5	4	0	100
1	12	5	Dry	2	2	2	0
1	12	1	Dry	2	1	1	50
1	6	5	Dry	4	4	0	100
1	6	1	Dry	4	3	1	75

## CONCLUSIONS

Thus it appears that the maximum dosage for ordinary lawn and golf-green grasses lies somewhere between 1 and 5 ounces per square foot and considerably above the former, while the minimum dosage for the white grub is about 1 ounce. Temperature is shown to exert a decided influence on the minimum dosage for the white grub (1 ounce at 65°F. and less than 1 ounce being necessary at 85°F. or above) and presumably also upon the maximum dosage for the plants. Effective work against the grub appears to require injections not much over 6 inches apart. The soil moisture must be medium (10 per cent) to wet (20 per cent) for good results in grub destruction. Wetting the

surface of the soil in cases when the moisture is dry (5 per cent) to medium (10 per cent) seems to increase the effectiveness of the treatment. The charge should be placed several inches below the point where the grubs are working.

In general it may be said that this study seems to show that the control of the white grub when it occurs in situations in which it cannot be reached practically by cultural methods may be effected by fumigation of the soil by means of carbon bisulfide. The combination of its effectiveness against the white grub, its non-poisonous effect on plants when used in small quantities, and the stimulating effect which small dosages have upon lawn vegetation, make it a promising means of control for the white grub. Its relatively high cost will prove a limiting factor.

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# THE OXIDIZING POWER OF SOIL FROM LIMED AND UNLIMED PLOTS AND ITS RELATION TO OTHER FACTORS'

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#### INTRODUCTION

In the spring of 1908 a group of forty ½0-acre plots were laid out on the New Jersey Agricultural Experiment Station farm for the purpose of studying the influence of lime and of fertilizers upon the soil and upon the crops. As shown by the report of Lipman and Blair (3) one-half of these plots have received various fertilizer and manurial treatments, together with lime applications, while the other half received the same treatment but without lime. Different amounts of lime have been added to another group of 28 plots, the checks being unlimed (5). For over ten years a careful record of yields of dry matter, nitrogen recovery and chemical changes in the soil have been kept for these plots. Biochemically, a study of the oxidizing power of these soils is of especial interest because the chemical analyses show that the limed plots have lost considerably more carbon than those which were not limed.

## HISTORY OF THE PLOTS2

Four of the plots which will be designated as 11A, 11B, 21 and 24 were selected for the biological work reported herein. The drainage of the field in which these plots are located appears to be quite uniform. The soil has been classified as a Sassafras loam. It contains a small amount of coarse gravel and has a maximum water capacity of 49.8 per cent. Those who selected the land for these plots (3) state that it had been used for general farming for many years and that it has not been limed for a long period, probably from 20 to 25 years.

Plot 11A receives an annual application of minerals, consisting of acid phosphate at the rate of 640 pounds, potassium chloride at the rate of 320 pounds and ammonium sulfate equivalent to 320 pounds of nitrate of soda per acre. Plot 11B receives a similar application, together with 4000 pounds per acre of ground limestone once in 5 years. Plots 21 and 24 receive annual appli-

<sup>&</sup>lt;sup>1</sup> Technical paper No. 4 of the New Jersey Agricultural Experiment Station, Department of Soil Chemistry and Bacteriology.

<sup>&</sup>lt;sup>2</sup> Prof. A. W. Blair has kindly submitted data for the crop and soil history of these plots and has also read the manuscript.

cations of acid phosphate, potassium chloride and sodium nitrate at the rates of 400, 200 and 200 pounds, respectively. In addition, plot 24 received ground limestone applications as in plot 11B. It should be stated that the first lime application (1908) was at the rate of only 2000 pounds per acre.

Plots 11A and 11B have been subjected to a 5-year rotation consisting of corn 1 year, oats 1 year, wheat 1 year and timothy 2 years. The rotation on plots 21 and 24 has been corn with vetch as a green-manure crop the first year, oats followed by cowpeas as a green-manure crop the second year, wheat the third year, and timothy and clover the fourth and fifth years. Thus

TABLE 1

The total dry matter during a 10-year period, in crops from limed and unlimed fertility plots

			T 11A		T 11B MED			OT 21 LIMED		OT 24 MED
YEAR	CROP	Grain	Hay, straw or stover	Grain	Hay, straw or stover	CROP	Grain	Hay, straw or stover	Grain	Hay, straw or stover
		lbs.	lbs.	lbs.	lbs.		lbs.	lbs.	lbs.	lbs.
1908	Corn	134.0	169.7	147.6	177.9	Corn	78.2	145.5	100.9	159.3
1909	Oats	24.5	100.4	14.5	104.5	Oats	16.6	59.7	22.2	73.6
1910	Oats	85.0	177.5	87.5	170.0	Wheat	50.0	92.5	72.3	132.5
1911	Wheat	75.0	97.5	85.0	110.0	Oats	42.5	62.5	50.0	75.0
1912	Timothy		146.3		120.0	Timothy aud clover		96.3		108.8
1913	Corn	130.0	100 F	255.0	310.0	Corn	85.0		167.5	
	00111	120010				00111				
1914	Oats	80.0		50.0		Oats	66.0		60.0	
1915	Wheat	128.0		160.0		Wheat	104.0		124.0	
1916	Timothy		240.0		408.0	Timothy and clover		380.0		600.0
1917	Timothy		192.0		354.0	Timothy and clover		262.0		350.0
	y matter	656.5	1625.9	799.6	2128.4		442.3	1573.5	596.9	2064.2
	increase over ed plots	20.2	30.9				34.9	31.2		

it is seen that the rotation on plots 21 and 24 has included legumes, while that on plots 11A and 11B has not.

The dry weights of the crops of these four plots for a period of 10 years or two rotations are given in table 1. With few exceptions, the annual yield of grain and of straw or of stover is higher on the limed than on the unlimed plots. When the total yields for 10 years are considered, the yields of grain on the limed plots 11B and 24 are greater by 20.2 and 34.9 per cent, respectively, than those of the unlimed plots 11A and 21. In the same way the yields of hay, straw and stover are 30.9 and 31.2 per cent greater on the limed than on the unlimed plots.

The average yield of dry matter of the 40 plots, which include plots 11A and 11B is about the same on the limed as on the unlimed plots. Lipman and Blair (4) state that "these experiments would seem to show beyond a doubt, that for the light coastal plain soils, lime has very little place in rotations which omit legumes." Plots 11A and 11B are the only ones of the above series to which ammonium sulfate was added. This explains why lime increased the crop yield, as the soil on plot 11A is now in a very poor condition.

Although lime has a marked effect upon increasing the dry weight of the crops, it does not influence the nitrogen content appreciably. The averages

TABLE 2

The percentage of total nitrogen, during a 10-year period, in dry matter of crops taken from limed and unlimed fertility plots

		PLOT	11A IMED		T 11B		PLOT UNL		PLO	r 24 fed
YEAR	. CROP	Grain	Hay, straw or stover	Grain	Hay, straw or stover	CROP	Grain	Hay, straw or stover	Grain	Hay, straw or stover
		per cent	per cent	per cent	per cent		per cent	per cent	per ceni	per cent
1908	Corn	1.48	0.95	1.42	0.97	Corn	1.31	0.50	1.29	0.59
1909	Oats	2.37	1.09	2.26	1.20	Oats	2.20	0.86	2.26	0.84
1910	Oats	2.04	0.58	1.95	0.65	Wheat	1.91	0.45	1.76	0.42
1911	Wheat	2.55	0.63	2.30	0.50	Oats	2.12	0.97	2.18	0.81
1912	Timothy		0.93		0.94	Timothy and clover		0.85		0.89
1913	Corn	1.52	0.82	1.48	0.88	Corn	1.21	0.57	1.44	0.82
1914	Oats	2.34	0.97	2.39	1.02	Oats	2.02	0.73	2.19	0.75
1915	Wheat	2.34	0.68	2.08	0.45	Wheat	1.97	0.30	1.99	0.28
1916	Timothy		1.09		0.83	Timothy and clover		0.87		1.20
1917	Timothy		1.03		0.76	Timothy and clover		0.76		0.85
Average p	per cent	2.09	0.88	1.98	0.82		1.82	0.67	1.87	0.75

for the 10 years show a slightly higher percentage for grain, straw and stover on one of the limed plots but not on the other (table 2).

Turning now to the effect of lime upon the soil itself, the chemical record shows (table 3) that the limed plots have lost considerably more carbon than the unlimed, for in 1917 the loss of carbon from plot 11B over plot 11A totaled 0.15 per cent of the soil weight, and from plot 24 over plot 21, 0.085 per cent. On the basis of 2,000,000 pounds of soil per acre this is a loss of 3000 pounds of carbon, or over 6000 pounds of organic matter in the one case and 1700 pounds of carbon, or over 3400 pounds of organic matter, in the second comparison, in which the rotation included legumes.

Timothy and clover were growing on the plots during the season (1916) when they were sampled for the tests given below. The limed soils were noticeably in the best physical condition, although lime had not been applied for the past five years. The vegetation looked best on plot 24, followed by 11B, 21 and 11A. Plot 11A had a very unfavorable appearance, being partly covered with patches of crab-grass. Its soil is unusually acid because of the annual applications of ammonium sulfate.

The above summary of the crop and soil history of these plots prepares the way for a better comprehension of the biochemical results obtained with the soil.

TABLE 3

Total carbon, total nitrogen and lime requirement of the plots in 1908, 1912 and 1917

		TOTAL NI	TROGEN			LIME REQUIREMENT				
PLOT NUMBER	1908	1912	1917	De- crease on limed plots	1908	1912	1917	De- crease on limed plots	1912	1917
	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	lbs.	lbs.
11A, unlimed.	11118	0.0977	0.0904	0.0085	1.216	1.140	1.210		2100	2000
11B, limed	\\ \\ \\ \	0.0801	0.0819	0.0085	§1.210 \	1.015	1.060	0.150	1500	1000
21, unlimed.	1.000	0.0771	0.0794		}1.130 {	1.030	1.170		1200	1200
24, limed	1040	0.0810	0.0901	0.0107	1.130	0.995	1.085	0.085	Neu-	Alka-
4									tral	line

#### EXPERIMENTAL METHODS

Sufficient soil was obtained in November, 1916, from each of the four plots to permit the use of fresh-soil methods. These bulk samples were composites of 12 individuals from the surface 6 inches after about \( \frac{1}{4} \) inch of the immediate surface had been scraped away. The samples were taken at a time when the soil was fairly dry and were sieved through a 5-mm. sieve, in the field, upon a piece of oilcloth and transferred to clean glass jars. Upon reaching the laboratory, portions of these samples were withdrawn for determinations of moisture and of the number of organisms. As soon as the moisture content had been ascertained, amounts equivalent to 200 gm. of oven-dry soil were weighed out into glass tumblers. Weighed amounts of organic matter were then added and mixed as thoroughly as possible with the soil. It is probable that the organic matter was not as well distributed as it would have been had the soil been dry. However, it seemed preferable to use the fresh, undried soil in order to approximate field conditions as nearly as possible. Finally, water was added to the extent of 50 per cent of the soil's maximum capacity. The tumblers were capped with petri dishes and incubated at 20° to 22°C. A similar set was used for the determinations of ammonia, nitrate and total nitrogen present at the beginning of the incubation periods.

Nitrates were determined by Allen's (1) reduction method, Devarda's alloy being used. Ammonia was determined by the magnesium oxide, and total nitrogen by the Kjeldahl method. Counts were made of the colonies appearing on Brown's egg albumim agar (2). The carbon-dioxide evolution was measured in an apparatus which has been previously used and described (6), except that the flat continuous base of the former apparatus was replaced by individual bases, grooved to receive the bell jars and sealed with paraffin (plate 1). Furthermore, the indrawn air was freed from carbon-dioxide by passing it through tubes containing \(\frac{1}{4}\)-mesh soda time (for carbon-dioxide determinations) instead of bubbling it through a potassium hydroxide solution. This caused the air pressure within the incubation chambers to be more nearly normal, which, together with a slow but continuous aspiration, made the conditions of the test approx mate those existing in the fields.

The carbon-dioxide determinations on the samples taken in 1916 are not reliable because of leaks in the apparatus. Those reported are on samples taken in October, 1919.

It should be noted that the only materials added to the soil for these tests were: water, 0.75 gm. of soybean hay (seeds and stems) per tumbler for the carbon-dioxide determinations, dried blood sufficient to contain 100 mgm. of nitrogen for the ammonia and nitrate tests, and 1 per cent of mannite to the soil incubated for a determination of nitrogen fixation. The periods of incubation are given in the tables.

#### THE OXIDIZING POWER OF SOIL FROM THE LIMED AND UNLIMED FERTILITY PLOTS

The oxidation activities of the limed soils were greater than those of the unlimed soils throughout the 16-day period during which the evolved carbon dioxide was collected (table 4). The largest amount came from the limed

TABLE 4

The production of carbon dioxide obtained from mixing 0.75 gm. of soybean hay with 200 gm. of soil from limed and unlimed fertility plots

DAYS INCUBATED	PLOT 11A UNLIMED	PLOT 11B LIMED	PLOT 21 UNLIMED	PLOT 24 LIMED	
	mgm.	mgm.	mgm.	mgm.	
0-2	51.4	87.0	55.8	109.7	
3-4	81.9	89.8	49.7	90.6	
5–8	87.1	142.5	93.2	132.8	
9–10	61.9	73.5	78.7	86.8	
11–16	70.1	112.8	111.5	122.1	
Total	352.4	505.6	388.9	542.0	
Per cent increase over the unlimed plots	43.7		39.3		

soil of plot 24. This is the only one of the four soils which reacted alkaline to the Veitch test. The smallest amount was obtained from the soil of the unlimed plot 11A, which soil gave the greatest lime requirement by the Veitch

method. Comparing plots 11A and 11B which have had identical treatments, except in the case of liming, it is seen that the oxidizing power of the limed soil was 43.7 per cent greater than that of the unlimed. In a similar comparison the carbon-dioxide production was 39.3 per cent greater from soil of the limed plots than from that of the unlimed plot 21. Thus these data show that the greater the lime requirement of a Sassafras loam the smaller is its oxidizing power.

As these carbon-dioxide determinations are a direct measure of the rapidity of loss of organic matter from these plots, it is of importance to note the correlation between these measurements and the analyses for total carbon which have been made on the soil (table 3), by which Lipman and Blair have shown (3) that the adding of lime has caused a considerably increased depletion of the organic matter originally present in the soil 10 years ago. Moreover, the above carbon-dioxide tests reveal the present oxidizing power of the soils and indicate that if organic matter were added, in a very short time it would largely disappear from the limed plots. These tests were made with the soil two summers after lime had been applied and therefore represent an average oxidation activity, assuming that this activity was greater during the season that lime was applied than during the season four years later, before the next application of lime.

# THE RELATION OF CARBON-DIOXIDE PRODUCTION TO OTHER MEASURES OF BIOCHEMICAL ACTIVITY

A measure of the ammonifying, nitrifying and nitrogen-fixing powers of a soil gives an indication of the nitrogen transformation possibilities therein, and merits consideration. A comparison of these factors with the carbon-dioxide production may be noted in table 5. Figure 1, which is based on this

TABLE 5

The production of carbon dioxide from soil of limed and unlimed plots as related to other biochemical factors

PLOT	CO2 PRODUCTION IN 8 DAYS	NHs-nitro- GEN ACCUMU- LATION IN 6 DAYS	NOs-NITRO- GEN ACCUMU- LATION IN 28 DAYS	NITROGEN FIXATION IN 20 DAYS	BACTERIAL NUMBERS	LIME TREATMENT
	mgm.	mgm.	mgm.	mgm.	millions	
11A	220.7	11.93	10.4	-0.02	2.5	None
11B	319.3	11.43	21.3	+1.35	6.2	2 tons per acre
21	198.7	11.37	16.1	-0.90	5.1	None
24	333.1	11.69	33.9	+7.00	6.5	2 tons per acre

table, shows that carbon dioxide-production, nitrate accumulation and bacterial numbers are considerably higher on the limed than on the unlimed plots. This is also true of the nitrogen-fixation values obtained but, although each of these values is the average of three or more determinations, a comparison

between the plots can not be made because the experimental error was in some cases greater than the differences found between treatments. The ammonia accumulation was nearly the same for all of the plots and did not correlate with the carbon-dioxide production.

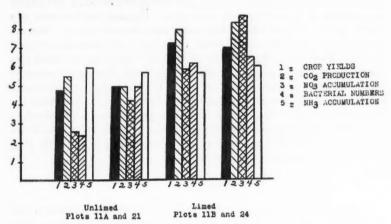


Fig. 1. A Comparison Between Crop Yields and the CO<sub>2</sub> Production, Bacterial Numbers, NH<sub>2</sub> and NO<sub>3</sub> Accumulation of Soil from Limed and Unlimed Plots

TABLE 6

Duplicate determinations of averages given in tables 4 and 5

PLOT NUMBER	CO <sub>2</sub> PRODUCTION	NH3-NITROGEN ACCUMULATION	NO3-NITROGEN ACCUMULATION	BACTERIAL NUMBERS	NITROGEN WITH MANNITE	FIXATION WITH- OUT MANNITE
	mgm.	mgm.	mgm.	millions	mgm.	mgm.
[]	322.0	11.81	11.4	1.9	9.10	8.82
111	382.7	12.05	9.2	3.1	8.82	8.54
11A				2.6	8.96	9.38
					8.68	
ſ	477.1	11.32	20.2	5.8	10.08	8.12
11B {	533.5	11.56	24.4	5.8	9.66	8.40
				6.9	9.24	8.40
	419.6	11.93	14.0	4.5	7.84	7.84
21	358.2	11.19	18.2	5.5	7.42	7.70
				5.3	7.84	7.84
	552.5	11.32	33.0	6.6	8.82	8.26
	531.3	12.04	34.8	6.5	8.54	8.54
24				Lost	8.40	8.40
					8.68	8.68

CROP PRODUCTION AS RELATED TO THE OXIDIZING AND NITRIFYING POWER
OF THE SOILS

The average increase in the dry weight of crops from the limed plots shows a marked relationship to the increased carbon-dioxide production and nitrate accumulation in the soil from the same plots. Bacterial numbers were also greater in the soil from which larger crops were obtained (fig. 1). But the relationship is especially close between crop yields and carbon-dioxide production. Thus the average increase in total dry matter on the limed plot 11B over the unlimed plot 11A is 28.3 per cent (table 2) and the increase in carbon dioxide production is 43.7 per cent. The corresponding increases for plot 24 over plot 21 were 32.0 and 39.3 per cent, respectively. When the percentage increase of crop production for the past 5 years is considered, it even more nearly approximates the percentage increase in carbon-dioxide production, as the differences between the crop-producing power of the plots were greater during the second rotation period.

#### CONCLUSIONS

If sufficient organic matter is present, the addition of basic substances, such as lime, generally results in a greater crop production and in a greater drain upon the soil. Assuming that the soil should not be allowed to become depleted in its supply of organic matter, the amount of liming to be done depends upon the balance between the cost of an increased feeding of the soil and the value of the increased crop production. Since plant growth is biological in nature, biological studies of a soil may possibly indicate its cropproducing possibilities more closely than purely chemical or physical studies—not considering fluctuating climatic conditions which are often the determining factors. This investigation gives evidence that future crop production may be indicated by a measure of the oxidizing and nitrifying power of the soil; and that some of the information as to what a soil needs in order to produce more, may be obtained from a manipulation of the same methods.

## SUMMARY

- 1. Fresh soils from the surface 6 inches of four  $\frac{1}{2^{1}}e^{-}$  acre fertility plots at the New Jersey Agricultural Experiment Station were tested for their oxidizing, nitrifying, ammonifying and azofying powers.
- 2. The oxidizing power of the soil from the limed plots was approximately 40 per cent greater than that from the unlimed plots.
- 3. For this soil type (Sassafras loam) the oxidizing power varies inversely with its lime requirement.
- Nitrate accumulation and bacterial numbers were higher on the limed soils whereas the ammonia accumulation was about the same for all of the plots.

5. The average crop yield for the past 10 years varies closely with the present oxidizing power of the soils. There is also a noticeable correlation between crop yield, nitrate accumulation and bacterial numbers, but not between crop yield and ammonia accumulation.

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## PLATE 1

Fig. 1. Illustration showing four of the twelve units of an apparatus used for determining the carbon dioxide produced by soil organisms.

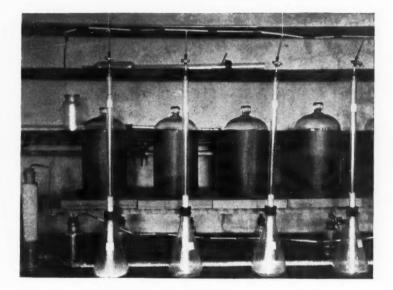
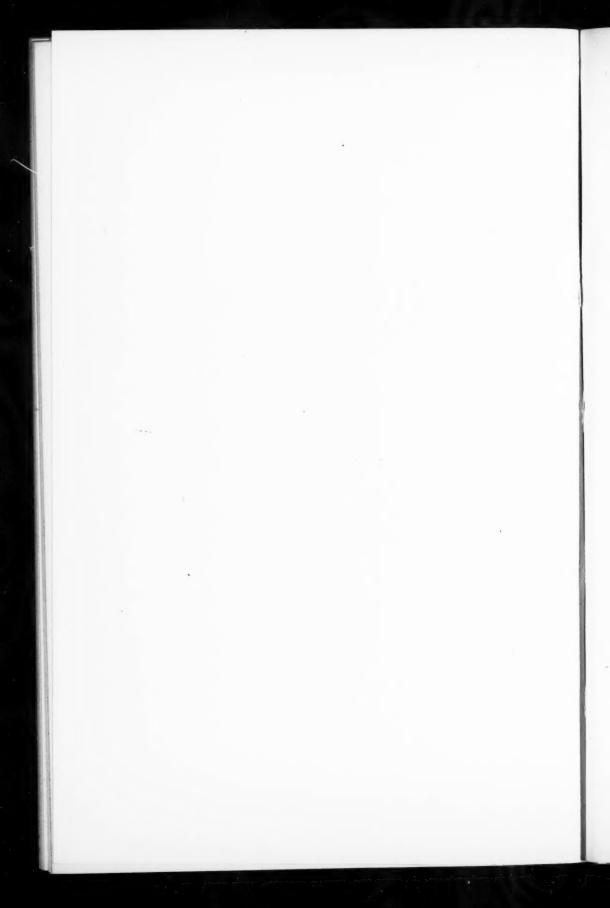


Fig. 1



# THE DETERMINATION OF CARBON DIOXIDE IN WATER-INSOLUBLE CARBONATES<sup>1</sup>

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The methods described in this article are modifications of two recently devised for biological work, the original apparatus and methods of procedure having been altered to render them suitable for use with such materials as limestones, marls and soils. For purposes of discussion they will hereafter be designated as (a) the titrimetric method and (b) the gasometric method.

#### THE TITRIMETRIC METHOD

This method was originally devised primarily for the determination of the carbonate content of bones, though it was pointed out that it could also be used for any carbonate-containing material. The following is the technic originally described.

The sample is weighed into a tube 20 to 25 mm. in diameter and placed in a 250-cc. suction flask containing an excess of 0.1N barium hydroxide. A one-hole rubber stopper holding a dropping funnel is then inserted into the mouth of the flask in such a way that the stem of the funnel projects into and somewhat below the top of the tube containing the sample. A short piece of heavy-walled pressure tubing holding a screw clamp is slipped over the side arm of the flask. When this tube and funnel are in place the flask is evacuated to a pressure of less than 50 mm. of mercury and the screw clamp closed. Approximately 1 N hydrochloric acid is then allowed to enter slowly through the dropping funnel, running down the inside of the tube and decomposing the sample of carbonate with the liberation of carbon dioxide which is absorbed by the barium hydroxide. When decomposition is complete the flask is rotated for three minutes or more to break up the surface film of barium carbonate and permit the complete absorption of carbon dioxide, after which the screw clamp is opened and the stopper, funnel and tube removed, the liquid adhering to the outside of the tube being washed back into the flask. The excess barium hydrate in the flask after being washed through a Gooch crucible to separate it from the precipitated carbonate, is titrated with 0.1 N HCl, with phenolphthalein as the indicator.

<sup>&</sup>lt;sup>1</sup> Journal article No. 16 from the Chemical Laboratory of the Michigan Agricultural College Experiment Station. Published by permission of the Director of the Experiment Station.

This technic without modification is quite suitable for the analysis of limestones and marls. Certain precautions however, are to be observed. We found, for instance, that the violent evolution of gas taking place when the first drop of acid came into contact with the dry sample caused some of the solid to be carried either out of the tube entirely or so far up onto its walls that complete decomposition was attained only with difficulty. This was obviated by covering the sample with water. This diluted the first few drops of acid to such an extent that the initial reaction was slowed down so that the subsequent evolution of gas could be regulated.

As a matter of routine the addition of a drop or two of octyl alcohol is also to be advised. Unless this is done a persistent froth forms frequently with marls and occasionally with limestones which makes it necessary to add acid very slowly. This materially lengthens the time required to complete a determination.

The minimum amount of wash water must be used in transferring the excess barium hydroxide to the titration flask and this wash water must be neutral to phenolphthalein. The whole procedure should be carried out as speedily as possible with the minimum exposure of the barium hydrate to the air. To facilitate this we use a disc of filter paper in the Gooch crucible instead of the usual mat of asbestos. This allows the filtration to be carried out rapidly. The carbonate is precipitated in such a form that there is no danger of its passing through such a filter. The technic of the operation can be checked from time to time by blank determinations in which the whole procedure is carried out with the omission of the sample.

For the analysis of soils, which, as a rule, contain so little carbonate that it is necessary to take samples of several grams, the above procedure must be modified because of the difficulty in obtaining a complete mixture of the sample and the acid in a small tube nearly full of solid. We have therefore reversed the relative position of alkali and sample, weighing the sample directly into the flask from a weighing bottle and placing the standard alkali in the tube. The stem of the dropping funnel is bent slightly to permit it to be placed in position *outside* of the tube and so admit the acid into the flask itself. In other respects the technic employed is the same as that followed above.

## THE GASOMETRIC METHOD (1)

This method was originally designed for the determination of CO<sub>2</sub> in blood plasma but was suitable for the analysis of all carbonates in solution. We have so modified the apparatus that it can be used equally well for materials in the solid form, the only changes necessary being a larger burette to hold the greater volume of gas produced from samples of high-carbonate materials of usual size and an opening of sufficient diameter to permit the introduction of such samples. Figure 1 shows the apparatus.<sup>2</sup>

<sup>&</sup>lt;sup>2</sup> The apparatus is being made by the Emil Greiner Company, 55 Fulton Street, New York.

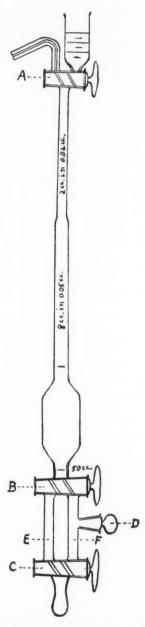


Fig. 1. Apparatus for the Determination of Carbon Dioxide in Insoluble or Undissolved Carbonates

It consists of a 10-cc. burette having the upper 2 cc. graduated in 0.02 cc. and the remaining 8 cc. graduated in 0.05 cc. The upper end of this burette is closed by a three-way stop-cock having one arm bent as illustrated and the other one sealed to a cup holding 5 to 10 cc. graduated to 5 cc. in 0.5 cc. The lower end of the burette is sealed to a bulb of such size that the whole apparatus will have a capacity of 50 cc. from the stop-cock A to a mark between the bulb and the stop-cock B. The openings in the stop-cocks B and C should be large, as mercury is forced through them.

The stopper D should be as close to B as convenient in order to reduce the space above it and the total capacity of the stopper and right-hand tube F to which the stopper is attached should be about 5 cc. The stopper should be hollow and the end should be open. It should be set at right angles to F.

The lower outlet of *C* is attached by a piece of heavy-walled suction tubing to a leveling bulb filled with mercury.

The following is the technic employed in making a determination. For marls, limestones or other materials so high in carbon dioxide that a sample of less than 500 mgm. will liberate not over 10 cc. of gas the hollow stopper serves as a weighing bottle and the material is weighed into it, the tube being filled with mercury up to the mouth of D to reduce the air space which must subsequently be evacuated. For carbonate-poor substances such as soils, the sample is weighed into the tube F, being introduced by means of a test-tube funnel.

The whole apparatus except the right-hand tube F between B and C (but including the right-hand hole in C) is then filled with mercury. With the stop-cock A closed and the connection open between B and C through the tube E, the leveling bulb is lowered to such a position that the mercury level drops below C, evacuating the burette, bulb, etc.<sup>3</sup> The cock B is then turned through a complete revolution establishing, as connection is made temporarily between them, equilibrium in gas pressure in the tube F and the evacuated space above it. The leveling bulb is then raised to a position above A and this cock opened, allowing the escape of the entrapped air. Repeating this operation several times reduces the air in the apparatus to a negligible amount. The sample is now held in a gas-free apparatus.

Approximately normal HCl is next poured into the cup above A and exactly 2.5 cc. admitted to the burette, the leveling bulb being held about even with the stop-cock B. The bulb is then lowered to the lowest position and the mercury allowed to flow out through the tube E, the cock B being closed while a little mercury still remains above it. If the sample is of such material that it is still contained in D, the mercury in the tube below it is now permitted to flow out through C, which is closed leaving a few drops above this cock to seal it. B is then turned to allow the acid to run into the tube F.

<sup>&</sup>lt;sup>8</sup> This is conveniently done by means of a heavy cord of proper length attached to the bulb by one end and by the other to the support holding the apparatus.

The sample, if not originally weighed into the tube, is shaken out of the stopper into the acid. No precautions need be taken to moderate the violence of the reaction as any particles of the sample carried up into the bulb will be decomposed later. The apparatus should be shaken so that all of the sample is washed out of the stopper D and down from the walls of the tube.

TABLE 1

Carbon dioxide indicated by reading of V cc. of gas after a single extraction

TEMPERATURE OF ANALYSIS	AIR DISSOLVED IN 2.5 CC. H <sub>2</sub> O SUBTRACT THIS FROM V AND MULTIPLY RESULT BY A TO CALCULATE MGM. CO <sub>2</sub>	A	TEMPERATURE OF ANALYSIS	AIR DISSOLVED IN 2.5 CC. H <sub>2</sub> O SUBTRACT THIS FROM VAND MULTIPLY RESULT BY A TO CALCULATE MGM. CO <sub>2</sub>	A
°C.	cc.	mgm.	°C.	cc.	mgm.
15	0.051	$\frac{B}{760} \times 1.935$	23	0.045	$\frac{B}{760} \times 1.842$
16	0.050	$\frac{B}{760} \times 1.924$	24	0.044	$\frac{B}{760} \times 1.831$
17	0.049	$\frac{B}{760} \times 1.912$	25	0.043	$\frac{B}{760} \times 1.819$
18	0.048	$\frac{B}{760} \times 1.900$	26	0.042	$\frac{B}{760} \times 1.808$
19	0.048	$\frac{B}{760} \times 1.889$	27	0.041	$\frac{B}{760} \times 1.796$
20	0.047	$\frac{B}{760} \times 1.877$	28	0.040	$\frac{B}{760} \times 1.784$
21	0.046	$\frac{B}{760} \times 1.866$	29	0.040	$\frac{B}{760} \times 1.773$
22	0.045	$\frac{B}{760} \times 1.854$	30	0.039	$\frac{B}{760} \times 1.761$

TABLE 1A

Values of  $\frac{B}{760}$ 

				700	_		
BAROMETER	B 760	BAROMETER	B 760	BAROMETER	B 760	BAROMETER	B 760
720	0.947	734	0.966	748	0.984	762	1.003
. 722	0.950	736	0.967	750	0.987	764	1.006
724	0.952	738	0.971	752	0.989	766	1.008
726	0.955	740	0.974	754	0.992	768	1.011
728	0.958	742	0.976	756	0.995	770	1.013
730	0.961	744	0.979	758	0.997	772	1.016
732	0.963	746	0.981	760	1.000	774	1.018

When the evolution of gas has stopped, the communication between the leveling bulb and F is opened and the stopper and tube completely filled with mercury up to the 50-cc. mark. B is then closed and the apparatus shaken with a rotary motion in such a way that the liquid is distributed in a thin

layer about the walls of the bulb until equilibrium between the gas in solution and that in the free space is attained. The liquid is next quickly drawn back into F, by lowering the leveling bulb and opening B which, however, is closed before any gas passes into it. C and B are finally turned to allow mercury to flow up into the burette through E while the acid is retained in F, the leveling bulb is raised until the mercury surface in it is on a level with that in the burette and the gas volume read. A fraction of a cubic centimeter of acid will unavoidably be held in the burette. This will cause no appreciable error in the results but care must be taken to read the gas volume at the surface of this liquid and not at the mercury surface, although it is the levels of the two mercury surfaces that are equalized.

The temperature and barometer readings should be noted at the time of reading the gas volume which affords sufficient data to permit the calculation of the weight of CO<sub>2</sub> obtained from the sample by means of the tables<sup>4</sup> 1 and

TABLE 2

Comparison of gasometric and titrimetric methods of determining carbon dioxide

SAMPLE	CARBON	DIOXIDE	SAMPLE	CARBON	DIOXIDE
	Gasometric	Titrimetric	5.12.22	Gasometric	Titrimetri
	per cent	per cent		per cent	per cent
Calcium carbonate	43.53	43.84	Limestone, No. 4	40.220	40.550
Limestone, No. 211	43.32	43.21	Marl ,	42.400	42.290
Limestone, No. 212	42.29	42.40	Soil, No. 5	0.015	0.014
Limestone, No. 213	41.25	41.69	Soil, No. 10	0.075	0.077
Limestone, No. 1	43.88	43.97	Soil, No. 16	5.000	4.860

1A. For a complete discussion of the principle of the method the reader is referred to the original article. Suffice it to say that it depends upon the generation of gas in a Torricellian vacuum, the measurement of that portion of the gas contained in a volume of 47.5 cc. in equilibrium with the gas dissolved in 2.5 cc. of water and the calculation of the total volume of gas from its known solubility in water at the temperature of the determination, correction being made for the air dissolved in the 2.5 cc. of water.<sup>5</sup>

Table  $\overline{2}$  gives the results of analyses of various materials made by the two methods.

The deciding factor in the selection of the method to be used is the magnesium content of the material under examination. For magnesium-free or low-magnesium limestones the gasometric method is much to be preferred. As the magnesium content increases, the rate of decomposition decreases so

<sup>4</sup> Partly taken from Van Slyke (1, p. 317 and 360).

<sup>&</sup>lt;sup>5</sup> This may however be determined for each analysis by introducing a few drops of alkali into the apparatus through the cup after reading the total volume of gas. The CO<sub>2</sub> will of course be absorbed leaving the air, the volume of which may then be read off after equalizing the mercury levels.

that with some samples of dolomite several hours are required for the complete decomposition of a 100 mgm.-sample. Under such circumstances the method of choice is, of course, the titrimetric one since the cost of the apparatus required for running several determinations simultaneously is small in comparison with that needed for making a corresponding number with the gasometric method.

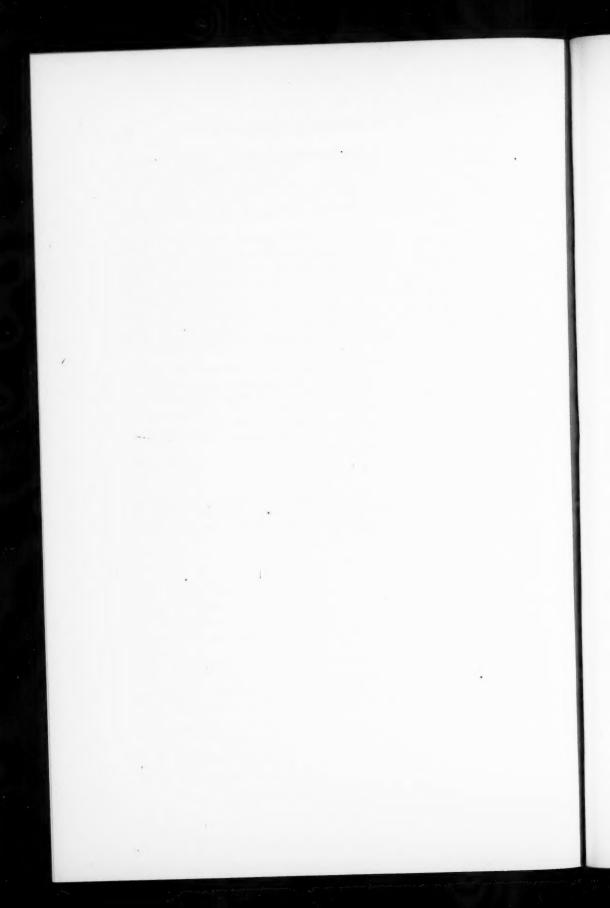
In this laboratory the gasometric method, however, has proven of great value for the rapid, routine, proximate examination of marls and limestones where great accuracy is not required. For this purpose the reaction is allowed to proceed for several minutes until the initial violence has subsided. With pure calcium carbonate this time is sufficient for the completion of the reaction and the results will be correspondingly accurate. With ordinary, low-magnesium materials they will be low in proportion to the amount of magnesium present. Ordinarily, where this does not exceed 5 per cent the error will be less than 2 per cent.

Of the two methods the gasometric one is the more accurate. The possible sources of error in it are fewer and the gas volumes can be read to 0.02 cc., or about 0.04 mgm. CO<sub>2</sub>. Assuming 0.05 cc. as the limit of accuracy for reading the titration values in the titrimetric method, the corresponding error would amount to approximately 0.1 mgm. CO<sub>2</sub>. This value of course, is augmented by errors introduced in transferring solutions from one flask to another, the absorption of CO<sub>2</sub> from the air, etc.

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# THE RELATION BETWEEN THE CALCIUM AND THE NITROGEN CONTENT OF PLANTS AND THE FUNCTION OF CALCIUM<sup>1</sup>

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The supply of calcium, especially in the carbonate form in the soil solution, becomes less as soils become more acid, and hence, in order to understand the relation of soil acidity to plant growth it is necessary to know something about the function of calcium in the metabolism of plants. One method of securing evidence regarding the function of an element is to observe the relations that exist between the amounts of this element and other elements or compounds that are present in different species of plants. In this way information may be obtained which indicates that either the element forms a part of certain compounds, or else it takes part in processes closely related to the formation or subsequent changes of the compounds. Both of these functions may, of course, be performed by an element. This brief preliminary paper sets forth the results obtained by applying this method of attack to the determination of the function of calcium, and reports a fairly close relationship between the calcium and the nitrogen content of plants, indicating that at least to some extent the use of nitrogen by plants involves the use of calcium.

## THE RELATIVE COMPOSITION OF PLANTS

In table 1 the composition of 34 species of plants is given with respect to nitrogen, calcium, phosphorus, magnesium, and potassium. These data were taken from the sources indicated, and are believed to be as reliable as any available. In the case of some plants the results of analyses of the different parts were found recorded without the weights of these parts. When this was the case estimates of the percentage of the total weight formed by the different parts were made and used in the calculation of the composition of the plant as a whole. The percentages of magnesium, phosphorus, and potassium were obtained from the sources indicated for calcium.

Figure 1 gives a graphic representation of the data of table 1 and is better for comparative purposes. The plants are arranged from left to right in the order of increasing percentages of nitrogen.

<sup>&</sup>lt;sup>1</sup> Published with the permission of the Director of the Wisconsin Agricultural Experiment Station.

TABLE 1
The composition of plants (dry-matter basis)

			Z	NITROGEN	-	0	CALCIUM		. RELATIVE AMOUNTS	TIVE		d	PER CENT	64
исивев	KIND OF PLANT	MATERIAL ANALYZED	Number of analyses	Reported	Per cent	Number of analyses	Reported	Per cent	z	Ca	EATIO OF CA	Magnesium	Phosphorus	Potassium
-	Sorghum (Sorghum vulgare, saccharatum)	Fodder	94	2	96.0	1	12	0.41	1.0	1.0	0.431	0.15	0.16	-
2	Meadow Fescue (Festuca pratensis)	Hay	21	N	1.23	4	2	0.44	1.0	1.0	0.360	0.11	0.16	1.78
	Water Grass (Paspalum laeve)	Hay	1	12	1.30	1	12	0.43	1.0	1.0	0.330	0.21	0.17	1.33
4	Red-Top (Agrostis vulgaris)	Hay	40	N	1.30	4	2	0.43	1.0	1.0	0.330	0.10	0.17	0.91
10	Timothy (Phleum pratense)	Hay	3	12	1.36	3	12	0.41	1.0	1.0	0.305	0.13	0.32	1.91
5	Corn (Zea mays)	Fodder	708	S	1.39	2	12	0.00	1.0	1.5	0.427	0.39	0.26	1.74
7	Orchard Grass (Dactylis glomerata)	Hay	46	N	1.42	4	2	0.38	1.0	1.0	0.252	0.20	0.20	1.66
00	Kentucky Blue Grass (Poa pratensis)	Hay	26	S	1.53	4	12	0.30	1.0	1.0	0.196	0.10	0.22	1.78
_	Oats (Avena sativa)	Fodder	24	N	1.62	6	12	0.38	1.5	1.0	0.234	0.14	0.30	2.67
10	Potatoes (Solanum tuberosum)	Ripe	1	12	1.73	36	12	0.55	1.5	1.5	0.318	0.30	0.29	1.74
11	Rye (Secale cereale)	Hay	38	S	1.92	-	12	0.38	2.0	1.0	0.197			
01	Bermuda Grass (Cynodon dactylon)	Hay	2	12	1.98	2	12	0.55	2.0	1.5	0.268	0.17	0.17	_
13	Barley (Hordeum sativum)	Fodder	-	12	1.99	1	12	0.69	2.0	2.0	0.348	0.16	0.43	3.15
14	Wheat (Triticum vulgare)	Fodder	15	S	2.11	7	12	0.34	2.0	1.0	0.163	0.00	0.32	2.67
15	Horse Radish (Cochleria armoracia)	Mature	1	12	2.13	-	12	0.71	2.0	2.0	0.335	0.15	0.34	2.90
16	Sugar Beet (Beta vulgaris)	Mature	86	12	2.23	-	12	0.65	2.5	2.0	0.295	0.39	0.23	2.07
17	Lupine (Lupinus hirsitus)	Half ripe	2	S	2.28	2	12	0.97	2.5	2.5	0.423	0.24	0.30	0.75
00	Onion (Allium cepa)	Mature	1	12	2.29	-	12	1.42	2.5	3.5	0.621	0.18	0.33	
19	Red Clover (Trifolium pratense)	In bloom	36	S	2.38	113	12	1.72	2.5	4.0	0.721	0.45	0.29	-
20	Alsike Clover (Trifolium hybridum)	In bloom	S	N	2.40	3	12	1.16	2.5	3.0	0.482	0.36	0.21	_
21	Sweet Clover (Melilotus alba)	Hay	18	S	2.53	-	2	1.39	3.0	3.5	0.548			
22	Mammoth Clover (Trifolium medium)	In bloom	1	10	2.56	3	12	1.49	3.0	3.5	0.583	0.58	0.22	2.57
23	Serradella (Ornithopus salina)	In bloom	-	10	05 6	-	13	1 20	2 0	2	0 520	010	0 42	2 65

24	Radish (Raphanus sativus)	Mature	-	12	2.64	1	12	12 1.50 3.0 3.5 0.568 0.28 0.33	3.0	3	5 0.5	899	0.28	0.33	2.49
25	White Clover (Trifolium repens)	Green	-	12	2.64	-	12	1.32	3.0	3	5 0.5	109	35	0.37	2.49
26	Cauliflower (Brassica oleracea, botrytis)	Mature	1	12	2.72	-	12	1.15	3.0	3.	0 0.4	123	35	0.26	2.98
27	Crimson Clover (Trifolium incarnatum)	In bloom	22	S		4	12	1	3.0	8	5 0.4	161	0.25	0.19	1.16
28	Rape (Brassica napus)	In bloom	37	5	2.78	9	12	1.	3.0	3.	0 0.4	147	0.10	0.43	2.15
50	Soybean (Glycine hispida)	Hay	23	5	2.80		4	1.96	96 3.0 5.0 0.718 0.74 0.32 0.	ı,	0 0.7	118	1.74	0.32	0.91
30	Vetch, common (Vicia sativa)	Green	14	S	2.98	25	12	1.39	3.5	3	5 0.4	167	32	0.33	1.91
31	Cowpea (Vigna unguiculata)	Hay	35	S	3.39		4	1.93	3 4.0	4	5 0.5	029	.45	0.24	0.83
32	Tobacco (Nicotiana tabacum)	Ripe	1	12	3.47	-	12	2.69	4.5	5.	0 0.7	99/	.48	0.42	3.06
33	Lettuce (Lactuca sativa)	Green	3	12	3.94	3	12	1.90	5.0	4	5 0.4	183	89.0	0.72	
34	Cabbage (Brassica oleracea, capitata)	Mature	2	12	4.02	2	12	12 1.90 5.0 4.5 0.472 0.36 0.53	5.0	4	5 0.4	172 (	36	0.53	

\* 59 analyses of tubers, 6 of tops. † 149 analyses of roots, 25 of tops.

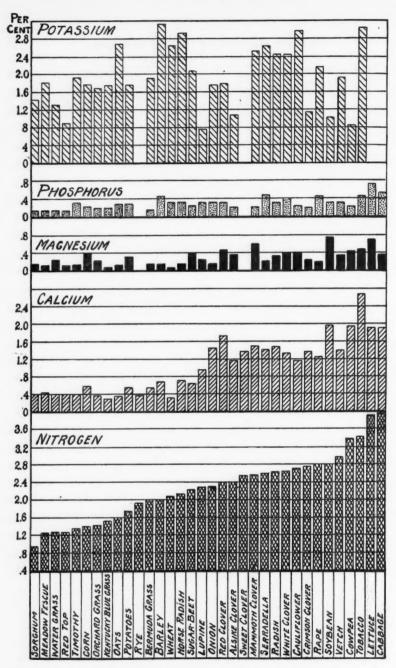


Fig. 1. Diagram Showing the Relation Between the Amounts of Nitrogen, Calcium, Phosphorus, Magnesium, and Potassium in the Plants Indicated

The outstanding feature of this figure is the relation between the calcium and the nitrogen content of the plants. The potassium content varies considerably, and there is no relation between it and the nitrogen content. Phosphorus increases with nitrogen, but to a much smaller extent. Phosphorus is not a constituent of all proteins, and therefore it need not necessarily vary with the nitrogen content. Furthermore, a considerable portion of the phosphorus usually exists in an inorganic form. According to the work of Ames and Boltz (1) approximately 50 per cent of the total phosphorus in the alfalfa plant is in an inorganic form. Hence, while there should be some relation between the nitrogen and phosphorus content, it need not necessarily be very close.

The magnesium content is more irregular and is relatively low in all cases. Its function being probably that of a phosphorus carrier, one would expect it to vary with the phosphorus and nitrogen, as it does in a very general way. Since the same magnesium may possibly be used over again for this purpose the total amount present need not necessarily increase regularly with increasing amounts of nitrogen and phosphorus.

#### THE RELATION OF CALCIUM TO NITROGEN

Calcium increases more regularly with increasing nitrogen than any of the other elements. There are marked variations, but since the data were taken from many sources, the results may not be strictly comparable in all cases. However, the data do indicate that there is a relation between the calcium and the nitrogen content of plants. For ease of comparison and in order to

TABLE 2

Range of nitrogen and calcium percentages according to relative figure

RELATIVE FIGURE	RANGE OF NITROGEN PERCENTAGES DESIGNATED BY RELATIVE FIGURE	RANGE OF CALCIUM PERCENTAGES DESIGNATED BY RELATIVE FIGURE
1.0	0 -1.30	0 -0.48
1.5	1.31-1.60	0.49-0.68
2.0	1.61-1.90	0.69-0.88
2.5	1.91-2.20	0.89-1.08
3.0	2.21-2.50	1.09-1.28
3.5	2.51-2.80	1.29-1.48
4.0	2.81-3.10	1.49-1.68
4.5	3.11-3.40	1.69-1.88
5.0	3.41 and above	1.89 and above

eliminate small irregularities due to various causes, relative figures of the nitrogen and calcium contents of the plants are included on the basis indicated in table 2.

The agreement of the relative figures is fairly good. In the case of plants high in nitrogen, the relative figures for calcium are usually higher than for

nitrogen. This is due to a higher ratio of calcium to nitrogen as indicated in the table. The ratios of calcium to nitrogen for the first seventeen plants as given in the table, are of the same order. The ratios of the last seventeen plants are of another order which is nearly twice as large as that of the first group. This indicates that the plants of the last group require nearly twice as much calcium for a given nitrogen content as do those of the first group. This relation is clearly shown in figure 1.

The plants are thus conveniently divided into two groups. The first group, having the average calcium-nitrogen ratio of 0.306 is composed almost entirely of members of the grass family, plants which as a class have a low lime requirement (11) and are quite tolerant to soil acidity. The second group, having an average ratio of 0.553, includes the legumes and plants which in most cases respond to liming and are sensitive to soil acidity. These data indicate an important difference in the metabolic processes of the two groups. Just what this difference is has not been determined definitely, but a possibility is indicated in the following discussion.

#### FUNCTION OF CALCIUM

Calcium functions in the plant in at least two ways. It serves as plant-food material and as such enters into the composition of proteins and other plant substances (8). In many plants, especially those high in calcium, a relatively small portion of the total amount is required for this purpose. A greater portion of the calcium taken up by the plant is probably used for the neutralization and precipitation of the acids in the plant sap (11). The carbonate and bicarbonate are the principal forms found in the soil solution that will perform the latter function. These forms after entering the plant react with the acids neutralizing them, liberating carbon dioxide. Oxalic acid is one of the strongest and more common of the plant acids. Reacting with calcium bicarbonate, it forms the neutral and insoluble calcium oxalate. Crystals of this oxalate are found in many plants.

The sources of plant acids are not definitely known. Many metabolic processes within the plant undoubtedly give rise to acids, some of which may be viewed as by-products. Some investigators hold that carbohydrate metabolism is an important source of plant acids. Protein formation involves reactions in which considerable amounts of acid may be produced. The decomposition of proteins in the life processes of plants offers many other possibilities for acid formation. The decomposition is probably brought about by oxidation, and as has been indicated by several investigators (10), the oxidation of protein produces acids among which are acetic, succinic, capronic, formic and oxalic.

Since a large portion of the calcium in many plants is used for the neutralization of acids, there should be more calcium in plants producing large amounts of acid. Assuming protein metabolism as an important source of

acids, a high protein or nitrogen content should be accompanied by a high calcium content. This conforms with the data presented in table 1.

As already indicated, the group of plants with a high calcium and a high nitrogen content also has a higher ratio of calcium to nitrogen. This may be partly due to the existence of poorer conditions for the complete oxidation and destruction of acids in this group, and hence the greater need and use of calcium carbonate for the neutralization of the acids. Since the conditions for oxidation in the different plants undoubtedly vary, an explanation is offered for the marked individual differences in the calcium-nitrogen ratio of certain plants. This explanation conforms with the suggestion of MacDougal, Richards, and Spoehr (9) that acid formation and accumulation in some plants may be due to poor oxidizing conditions within the plant tissue. On this basis, poor conditions for oxidation in plants increase the need for calcium in the carbonate form. There are, of course, a large number of other possible factors that may affect this need, and hence the ratio of calcium to nitrogen: e.g., the varying amounts of nitrogen in other than protein form may affect the calcium-nitrogen ratio to an appreciable extent in some cases.

The relation of calcium to nitrogen and important plant compounds and processes needs to be more carefully investigated with the more refined methods which have been devised in recent years. Undoubtedly, if a large number of different plants were grown with different soil treatments and then analyzed at various stages for calcium and different constituents and conditions, much extremely valuable information would be obtained regarding the relation of these to plants. In this connection the publications of Burd and Hoagland regarding some of these relations should be mentioned (3, 6, 7).

### SUMMARY

- 1. There is a rather close relation between the calcium and nitrogen content of plants.
- 2. The contents of potassium, phosphorus and magnesium do not bear this close relation to the nitrogen content.
- 3. The important agricultural plants may be divided into two groups; viz., (a) those having a low calcium-nitrogen ratio and a low lime requirement, and (b) those having a high calcium-nitrogen ratio and a higher lime requirement.
- 4. Protein metabolism is probably one of the chief sources of plant acids and this may give rise to the need of calcium in the carbonate form for the neutralization of these acids.

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## THE EFFECT OF DICALCIUM SILICATE ON AN ACID SOIL1

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At the meeting of the American Chemical Society at Boston in 1917 Cowles (1) and Scheidt presented experimental data with plants from which they concluded that dicalcium silicate has a greater value than either ground limestone or calcium hydrate as a fertilizer material, and that silicon is an essential element and promotes plant growth.<sup>2</sup>

Upon the solicitation of Mr. Cowles, who desired to have the work repeated with other soils and under other conditions, advantage was taken of an opportunity afforded in connection with an experiment conducted for another purpose, to include "dicalcium silicate" and "hydrated silica," prepared by the Electric Smelting and Aluminum Company, Sewaren, N. J., of which Mr. Cowles is president.

According to Mr. Cowles, 75 to 80 per cent of the dicalcium silicate may be considered as having the composition of (CaO)<sub>2</sub>SiO<sub>2</sub>, the remainder being zeolitic material composed of sodium, calcium, aluminum and silicon which has resisted the solvent action of boiling water for an hour. The following analyses accompanied the material:

iO <sub>2</sub>	per cent
$\mathrm{iO}_2$	. 28.70
l <sub>2</sub> O <sub>3</sub>	. 6.27
'e <sub>2</sub> O <sub>3</sub>	
aO	. 46.81
ИgO	. 2.94
O <sub>2</sub> and H <sub>2</sub> O	. 6.93
Na <sub>2</sub> O	. 6.47
	100.00

It is the leached residue of a sinter produced from a mixture of silicates, lime and sodium carbonate in the manufacture of disodium aluminate.

The hydrated silica was reported as having the following composition:

	 55.90
H <sub>2</sub> O	
Na <sub>2</sub> SO <sub>4</sub>	 4.09

<sup>&</sup>lt;sup>1</sup> Contribution 271 from the Rhode Island Agricultural Experiment Station at Kingston.

<sup>&</sup>lt;sup>2</sup> Results published by the Electric Smelting and Aluminum Company, Sewaren, N. J.

The Miami silt loam which was used in the pot experiment involving these materials was taken near the Rhode Island Agricultural Experiment Station plats and had been in turf for many years without manurial treatment. Fifteen pounds of the soil containing 18 per cent moisture were used in each 8-inch Wagner pot.

The alkaline materials and the largest applications of acid phosphate were added on May 6, 1919, so that they could react with the soil prior to the addition to each pot, on May 24, of the following basal fertilizer:

	grams
Nitrate of soda	1.5
Sulfate of potash and magnesia	5.0
Acid phosphate	3.5

On July 5, 1 gm. each of nitrate of soda and sulfate of potash was also added.

Cos lettuce was planted on May 26, but in some cases more seed had to be added on June 6. On July 3, final thinning was made to 6 plants per pot. Where plants of the first seeding had to be supplemented by those of the second seeding a somewhat uneven growth resulted, and the parallelism from duplicate pots was less satisfactory than it would have been had there been always the same proportions of plants from the first and second seeding. It is believed, however, that conclusions are warranted, even though the results are not closely quantitative. The crop was harvested on July 22.

The special applications in addition to the basal fertilizer, and the yields resulting from them, are given in table 1.

It may be seen that where only the basal application of fertilizer was applied without any other additions (pair 1), the lettuce made only a very small growth. Pairs 9, 10 and 11 show that maximum growth was attained by different proportions of calcium carbonate and acid phosphate, and even by a very large application of acid phosphate (pair 13). If desired to estimate the applications on an acre basis, it may be observed that 7.25 gm. per pot is equivalent to 1 ton per acre. It was shown by other pots that the basal fertilizer supplied enough for nutrient purposes.

Concerning an investigation described by the authors in another paper (2) the following statement was made at the close: "The results indicate that the practical advantage of phosphating and liming may often prove to be due to the precipitation of active aluminum quite as much as to supplying phosphorus as a nutrient, and lime as a reducer of acidity."

By comparing pairs 2 and 3 it appears that the dicalcium silicate corrected the condition about equally with an equivalent amount of limestone. Full opportunity was given for each to exert its maximum effect, as shown by the fact that in pair 4, 50 per cent additional limestone increased the growth.

There were no indications that the silicon in the dicalcium silicate was of any value. The same is true of the silicon in the hydrated silica, as may be seen by comparing pair 5 without—and pair 6 with—hydrated silica; or again,

pair 7 without—and pair 8 with—hydrated silica. The smaller yield in one of pair 7 seems to be attributable to the fact that five of the six plants were the partially developed ones of the second planting previously referred to.

The dicalcium silicate was as effective as limestone in counteracting the toxic conditions existing in the acid soil, but there was no evidence that there is any justification in claiming an additional value because of its content of silicon.

TABLE 1

Yields of dry cos lettuce leaves from duplicate pots, with the extra applications in addition to the basal fertilizer

PAIR	EXTRA APPLICATIONS	YIELDS OF DRY LETTUCE LEAVES
		gm.
1	None	
		4.5
2	Dicalcium silicate, 20.29 gm	
		13.0
3	Limestone, 20 gm., equivalent to the above	
		12.0
4	Limestone, 30 gm	15.0
-	T*	18.5
5	Limestone, 5 gm	11.0
6	Limestone, 5 gm.; hydrated silica, 7.25 gm. (1 ton per acre)	
U	Elinestone, 5 gm.; hydrated sinca, 7.25 gm. (1 ton per acre)	10.0
7	Limestone, 5 gm.; acid phosphate, 16.5 gm	
•	nimestone, o gin., acid phosphate, 10.0 gin	18.0
8	Limestone, 5 gm.; acid phosphate, 16.5 gm.; hydrated silica, 7.25 gm	
		20.0
9	Limestone, 5 gm.; acid phosphate, 26.5 gm	20.0
		21.0
10	Limestone, 10 gm.; acid phosphate, 11.5 gm	19.0
		19.0
11	Limestone, 15 gm	
		10.0
12	Limestone, 15 gm.; acid phosphate, 6.5 gm	
		19.0
13	Acid phosphate, 100 gm	21.0
	*	23.0

Even if it should ever be proved that, contrary to the opinion now generally held, silicon is an essential element, it seems probable that there would be enough of it active in our siliceous soils to satisfy all needs.

It should occasion no surprise if silicon were to have an advantageous indirect effect under conditions which were not shown to be optimum. If such an effect were observed, however, it would, obviously, be no proof that silicon is essential to plant growth.

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# MISCELLANEOUS SOIL INSECTICIDE TESTS

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The practical control of insects which spend the whole or a greater part of their lives underground has been in the past and continues to be a most difficult problem. In America we have depended almost entirely on agricultural practices for the control of soil-inhabiting insects, particularly those attacking field crops. Some years ago apparently successful experiments were conducted against white grubs in lawns with kerosene emulsion (1) but subsequent tests by other entomologists were so conflicting that the use of kerosene emulsion has never become general, although frequently advocated in literature.

Carbon bisulfide has been recommended for the grape Phylloxera, grub worms, and other underground insects in Europe and especially in France, and has been suggested by writers in America, but like kerosene emulsion it has never come into general use. More recently (8) carbon bisulfide has been found to be quite effective for destroying the woolly aphis and data at hand indicate its practical usefulness against other underground pests. Its use for general crop pests such as white grubs seems impractical, however, as was illustrated in a series of experiments conducted by W. H. W. Komp, a senior student at Rutgers College and working under the direction of Dr. Thos. J. Headlee (6). He found that common white grubs (Lachnosterna sp.) in lawns could be controlled by injecting carbon bisulfide into the soil at the rate of approximtely \(\frac{3}{4}\) ounce to the square foot which would cost, at 10 cents a pound, \$272 per acre, an amount prohibitive except for very intensively cropped land or very small areas. These experiments were not sufficiently comprehensive for conclusive results and, furthermore, the bisulfide was injected to a depth of only 3 inches, which condition would probably not permit a maximum diffusion of the gas. Our own experience with carbon bisulfide indicates that its use against most white grubs and similar insects is impractical, but that it can be used to advantage to destroy ant colonies and to kill grubs which have an open burrow, such as grubs of the southern green Tune beetle (Cotinis nitida).

More recently the cyanides—sodium cyanide, potassium cyanide, and hydrocyanic acid—have come into prominence as effective and practical for the control of many underground pests. The pioneer work with sodium cyanide as a soil insecticide should probably be attributed to J. A. Hyslop

of the United States Bureau of Entomology and F. A. Kaufmann of the Roessler and Hasslacher Chemical Company. Hyslop's experiments in 1913 (7) showed that commercial sodium cyanide (39 to 40 per cent cyanogen) applied dry in hills of corn or potatoes at the rate of 300 pounds per acre, will kill wireworms and not injure the soil permanently but that it cannot be applied with safety to crops while the crops are on the land or immediately prior to seeding. Although Kaufmann's results were not recorded in literature, as early as October 1915 he issued a mimeographed statement of his experiments which was distributed generally to entomologists, and his results were the basis for trying out cyanide against the Japanese beetle grub. In this mimeographed statement Kaufmann records the effective use of granular sodium cvanide in solution to destroy ants and white grubs (presumably Lachnosterna sp.) at a strength which will not ordinarily injure grass. The strength advised is a ounce of sodium cyanide to 1 gallon of water, this amount to be sprinkled over an area of about 6 square feet (5611 pounds in 7260 gallons of water per acre) which is afterwards thoroughly watered.

A carefully planned series of experiments were made by Peterson (10) for the control of wireworms with sodium cyanide and his results show that while these insects can be killed with large quantities of cyanide the amount necessary (300 pounds per acre) to bring about control makes it too expensive for ordinary use. Within the past few months, results of experiments with sodium cyanide for the control of the peach borer have been published (2). In this case the writer concludes from his experiments that this material is unreliable because, on account of its solubility under varying conditions, it often proved injurious to trees. The experiments are not reported in detail but one might infer that under certain prescribed conditions cyanide could

be used effectively and without injury to peach trees.

Experiments conducted in 1914 and 1915 with calcium cyanamide (45 per cent CaCN<sub>2</sub>) against the root-knot nematode by J. R. Watson led him to conclude (11) that this material applied at the rate of from 1 to 3 tons per acre and thoroughly mixed with the soil reduced the number of nematodes to an extent sufficient to permit profitable growing of susceptible plants. Injurious effects of the cyanide to newly planted crops persisted for a number of months in some cases. Sodium cyanide was found to be a satisfactory control for this nematode according to the experiments conducted and reported by W. P. Duruz (4). He reports "nearly a perfect control" in greenhouses when two applications were made at the rate of 200 pounds of sodium cyanide in 14,520 gallons of water per acre for each application. Moist warm soil and aeration by occasional stirrings were necessary for the best results. Seeds of such plants as tomato, radish and cucumber germinated satisfactorily when planted a week after the last treatment. Another series of experiments recently recorded by L. P. Byars (3) shows that sodium cyanide (2 parts) and ammonium sulfate (3 parts) applied at the rate of 3600 and 5400 pounds per acre failed to eradicate completely the root-knot nematode and the author concludes that the method is not practical against this nematode although it seemed to be more efficient than most chemicals which have been tried. There seemed to be no difference in effectiveness when applied dry and as a liquid.

Comprehensive and valuable data on cyanide gas as a soil fumigant have been obtained and reported by E. R. de Ong (9). His experiments were conducted to determine the effect on plants, diffusion in soil, etc., rather than to determine the effect on insects and with applications in gaseous form rather than in liquid. His most important conclusions from our point of view were that "a heavy damp or a very wet sandy soil is almost impervious to hydrocyanic-acid gas" and that "gas generated in a soil body diffuses with extreme slowness in clay soils or very wet sandy soils, but in sand with a medium amount of moisture, diffusion of gas is much more rapid." He concludes that "sodium cyanide offers a satisfactory means of fumigating masses of loose, porous soil, especially those with only small amounts of clay, or of seed-beds and potting soil" and that "such treatments allow of much wider range of concentrations when the soil is not occupied by a crop."

The author wishes to review here his own brief experience with the more common soil insecticides.

#### KEROSENE EMULSION

Kerosene emulsion has been repeatedly recommended for various kinds of underground insects but very few experiments have been made to affirm or disprove its value. In 1888 W. B. Alwood tested kerosene emulsion against

TABLE 1

Results with kerosene emulsion against Popillia grubs, Riverton, N. J.

	R.	ATE PER A	CRE	ED	INED			RES	ULTS			REST	ULTS	
CHARACTER OF FIELD	Kerosene	Amount	Additional	AREA TREATED	AREA EXAMINED	DATE TREATED	DATE EXAMINED	Dead	Alive	KILL	DATE REEXAM- INED	Dead	Alive	KILL
	per cent	gal.	,	sq. ft.	sq. ft.	1919	. 1919			per ceni	1919			per cens
Thin weeds	8	10,450	None	100	9	Sept. 15	Sept. 22	48	76	38.7+	Sept. 25	26	20	54.3+
and grass	4	20,900	None	100	9	Sept. 15	Sept. 22	45	77	36.8+	Sept. 25	15	32	31.9+
Timothy	8	10 450	None	100	9	Sept. 18	Sept. 22	1	3	25.0	Sept. 23	2	4	33.3+
stubble	4	20,900	None	100	9	Sept. 18	Sept. 22	3	13	18.7+	Sept. 23	0	14	0

the white grub of the southern green June beetle (*Cotinis nitida*) on the Capitol grounds at Washington, D. C., with apparent success. However, his statements are contradictory to the life history of this species of grub and it therefore appears likely that other grubs were present and confused his conclusions. A few years ago the writer had an opportunity to test out kerosene

emulsion against grubs of *Cotinis* on a golf green at Louisville, Ky. An 8 to 10 per cent emulsion was found to be quite effective in destroying 80 per cent of these grubs when applied in August at the rate of 1 gallon to 6 or 8 square feet (5445 to 7260 gallons per acre) and afterwards throughly washed in with water. A slight browning of the tips of the grass was the only injury to the grass when the treated area was afterwards sprinkled with water. Against grubs of the green Japanese beetle (*Popillia japonica*) we obtained a kill of 25 to 54 per cent (table 1) when an 8 per cent kerosene emulsion was used at the rate of 1 gallon to 4 square feet (10,890 gallons per acre). In the same series of tests against *Popillia* grubs sodium cyanide has always given an appreciable better kill than the emulsion. We conclude that, as a rule, kerosene emulsion is not as satisfactory a soil insecticide as is cyanide because it is less effective, more expensive and more difficult to make up and apply.

### COAL TAR OR CREOSOTE PREPARATIONS

Emulsifiable coal tar or creosote preparations which are essentially composed of coal-tar oils, 53 per cent (percentages approximate); phenols, 12 per cent; water 10 per cent; and a saponifying agent, 25 per cent, are little known as soil insecticides. Our own experience with "Carco," a commercial preparation, and Barrett's disinfectant (sold only for disinfecting purposes but analyzing about the same as "Carco," giving equal insecticide results and very much cheaper) has not been extensive but we did find that it killed grubs of the green June beetle, being only slightly less effective than kerosene emulsion when diluted 1 to 125 parts of water and applied the same as the emulsion, that is, 1 gallon of diluted mixture to 6 or 8 square feet and afterwards sprinkled with water. The creosote mixtures brought a large percentage of the green June beetle grubs to the surface where they died; but kerosene emulsion is apparently a more rapid killing agent, as the dead grubs are more often in the soil although a few do come onto the surface before they die. We have repeatedly tested Barrett's disinfectant against the green Japanese beetle grub and the recorded results are given in table 2.

As a soil insecticide against the commoner white grubs it appears to be equal to kerosene emulsion but not as good as sodium cyanide.

#### MISCELLANEOUS TESTS

Corrosive sublimate. Repeated tests have proven the ineffectiveness of corrosive sublimate against our common white grubs.

Sulfuric acid. According to reports sulfuric acid has been used with apparent success against white grubs, in Europe. We tested it against the Japanese beetle grub, using it at the strength of 1 of acid to 96 of water, 1 to 48, and 1 to 24, applying 2616, 1308 and 872 gallons of diluted solution, respectively, per acre, but with none of these applications could we get better than a 10 per cent kill.

TABLE 2
Results with Barrett's disinfedant against Popillia grubs, Riverton, N. J.

	RAI	RATE PER ACRE	CRE					RES	RESULTS	
CHARACTER OF FIELD	Bar- rett's disin- fectant	Water	Addi- tional water	AREA	AREA EXAM- INED	DATE OF TREATMENT	DATE OF EXAMINATION	Dead	Alive	KILL
	gal.	gal.		sq.ft.	.1f.bs	6161	6161			per cent
Timothy and bluegrass	54.5	2616	Yes	100	6	Oct. 15	Oct. 20	15	26	36.6
2. Timothy and bluegrass	54.5	5232	Yes	100	6	Oct. 15	Oct. 20	00	11	42.1-
3. Timothy and bluegrass	54.5	7848	Yes	100	6	Oct. 15	Oct. 20	22	37	37.3-
Timothy and bluegrass	54.5	5232	No	100	6	Oct. 22	Oct. 27	6	15	37.5
5. Timothy and bluegrass	81.7	5232	No	100	6	Oct. 22	Oct. 27	00	9	57.1+
Timothy and bluegrass	54.5	5232	Yes	100	6	Oct. 22	Oct. 27	9	10	37.5
Timothy and bluegrass	54.5	5232	No	100	6	Oct. 29		S	2	71.4-
8. Timothy and bluegrass	81.7	5232	No	100	6	Oct. 29		8	3	50.0
Timothy and bluegrass	54.5	5232	Yes	100	6	Oct. 29		1	0	100.0
10. Bluegrass lawn.	54.5	5232	Yes	100	4	Oct. 30	Nov. 3	50	35	45.3-
. Heavy bluegrass	54.5	9269	Yes	100	4	Oct. 31	Nov. 4	1	r)	16.7-
2. Heavy bluegrass.	81.7	9269	Yes	100	4	Oct. 31	Nov. 4	1	9	14.3-

Note: "Carco" was used in Nos. 11 and 12. Depth of grubs at this season and heaviness of sod accounts for the low per cent of mortality. In plot 10, 51 of the grubs were Cyclocephala and 13 Popillia. None of the latter and 56.8+ per cent of the former were killed by the treatment. All of the Popillia grubs were 4 to 6 inches below the surface at the time of treatment. Acetaldehyde was used against the green Japanese beetle grub in varying strengths up to 1 to 48 of water at the rate of 5232 gallons of diluted solution to the acre, and 1 to 96 at the same rate per acre. It was wholly ineffective in a number of tests and the very best kill was less than 12 per cent.

Kopper's solution. A by-product received from the Kopper's Company and reported to analyze approximately 25 per cent carbon bisulfide and 75 per cent benzene gave negative results when used at a dilution of 1 to 48 and 5232 gallons of diluted solution to the acre, the best kill of a number of tests being 9 per cent.

### SODIUM CYANIDE

Among the important considerations in determining methods of controlling the Japanese beetle were methods of destroying the insect in the grub stage since the greater part of its life is as a grub in the ground. Mr. Goodwin, at the time in charge of the control operations, conducted numerous experiments, as reported at the last annual meeting of the American Association of Economic Entomologists (5), obtaining a kill of 65 to 90 per cent of the grubs where sodium cyanide was used in solution at the rate of approximately 110 pounds in 26,000 gallons of water, per acre. The past spring a considerable area infested by the grubs was treated according to this formula, but later counts showed that the kill averaged not over 25 per cent for the season. Experiments conducted by the use of a hand sprinkler gave far better results and a careful study of the conditions clearly indicated that the low mortality was due, not so much to the material used as to the method of application which in this case did not allow sufficient penetration. Accordingly, the sprinkler pipes for use the past fall were modified and as a result the cyaniding operations, which have been in charge of Mr. C. H. Hadley, on the 32 acres treated have given an average kill of about 80 per cent, the average up to the latter part of October being about 90 per cent but rapidly dropping off as the cold weather set in. Granular sodium cyanide was used at the rate of 165 pounds in 12,000 gallons per acre. Plate 1 illustrates the two types of sprinklers referred to above, the one (fig. 1) having 1-inch holes 10 inches apart, while the other (fig. 2) has \(\frac{3}{6}\)-inch holes averaging 48 holes to the foot, the pipe in both cases being 3-inch.

Two methods of applying the liquid sodium cyanide were used. For small-plot tests of one to several hundred square feet the ordinary sprinkling can, with the holes enlarged to about  $\frac{8}{32}$ -inch in diameter, was employed. This method is applicable for small areas such as lawns and home gardens. For large areas of one-half to ten or twenty acres 600-gallon tanks mounted on heavy wagon frames and drawn by a caterpillar-type tractor were used. These were fitted with perforated pipes as described above and illustrated in plate 1, figure 2. The flow was by gravity and regulated by a gate valve which could be operated by the driver of the tractor. The water supply was obtained from nearby creeks by means of a centrifugal pump and pipe line

rable soft softium cyanide against Popillia grubs, tank applications, Riverton, N. J.

		RAIE PER ACKE	ACKE	ABEA	NUMBER			RESULTS	TIL	
CHARACTER OF FIELD	NaCN	Water	Additional	TREATED	EXAM- INED	DATE TREATED	DATE EXAMINED	Dead	Alive	KILL
	lbs.	gal.	gal.	acres	sq. yd.	1919	6161			per cent
1. Robert's timothy stubble	220	8,000	None	0.3	3	Sept. 16	Sept. 20	30	1	+1.96
2. Robert's timothy stubble	220	Dry	8,000	0.3	3	Sept. 17	Sept. 20	16	15	51.6+
3. Robert's timothy stubble	165	8,000	None	0.3	3	Sept. 16	Sept. 20	41	1	49.76
4. Robert's timothy stubble	165	Dry	8,000	0.3	3	Sept. 18	Sept. 20	18	6	+9.99
5. Robert's timothy stubble	110	8,000	None	0.2	2	Sept. 13	Sept. 20	16	2	88.84
6. Bailey's hay stubble	165	12,000	None	11.0	16	Oct. 7	Oct. 9	98	45	65.6+
7. Jessup's old hay stubble	165	11,000	None	3.0	10	Oct. 20-21	Oct. 24	240	4	84.5+
8. Jessup's new hay stubble	165	11,000	None	2.0	12	Oct. 21-22	Oct. 25	165	12	93.2+
9. Robert's rye stubble	165	11,000	None	4.0	6	Oct. 6-9	Oct. 9	9	2	54.5+
10. Bailey's hay stubble	110	12,000	None	0.1	3	Sept. 21	Sept. 25	16	S	76.1+
11. Bailey's hay stubble	165	12,000	None	0.1	3	Sept. 21	Sept. 25	56	S	85.2+
12. Bailey's hay stubble	220	12,000	None	0.1	3	Sept. 21	Sept. 25	59	7	+4.96
13. H. Lippincott pasture	110	12,000	Watered	0.1	3	Oct. 30	Nov. 4	10	2	83.3+
14. H. Lippincott pasture	110	12,000	Rain	0.1	3	Oct. 30	Nov. 4	12	0	100.0
15. H. Lippincott pasture	165	12,000	Rain	0.1	3	Oct. 30	Nov. 4	11	2	84.6+
16. H. Lippincott pasture	165	12,000	Rain	0.1	3	Oct. 30	Nov. 4	3	0	100.0
17. H. Lippincott pasture	110	12,000	Watered	0.1	3	Nov. 4	Nov. 7	24	6	72.7+
18. H. Lippincott pasture	110	12,000	None	0.1	3	Nov. 4	Nov. 7	20	4	83.3+
19. H. Lippincott pasture	165	12,000	Watered	0.1	3	Nov. 4	Nov. 7	20	9	+6.97
20. H. Lippincott pasture	165	12,000	None	0.6	9	Oct. 30-	Nov. 13, 18	46	41	52.8+
						Nov. 7				
21. H. Lippincott pasture	165	12,000	None	0.5	S	Nov. 7-10	Nov. 17	10	16	38.4+

In plot 7 one square yard examined gave 6 dead and 30 live grubs. This examination was near the edge of the field and because of the low kill in this particular instance the percentage of mortality was appreciably lowered, the per cent of kill without this count being 94.3+.

Low mortality in plot 9 can be accounted for by the matted condition of the wild growth, preventing thorough penetration.

In plots 13 to 21 there were a few Lachnosterna grubs and in a few cases these were not distinguished from Popillia grubs. In plot 13 six of

the grubs were Lacknosterna, all of which were dead. In plot 17, seven were Lacknosterna, 85.7+ per cent of which were dead and in plots 18 and 19, four and one, respectively, were Lachnosterna, all of which were dead.

In plot 20 only the areas treated November 6 and 7 were examined. The grubs were 3 inches or more below the surface and the In plot 21 the grubs were 2½ to 5½ inches deep and the soil temperature below 48°F. temperature of the soil 48°F. or lower.

TABLE 4
Results with sodium cyanide against Popillia grubs, sprinkler applications, Riverton, N. J.

		RATE PER ACRE	ACRE	AREA	NUMBER			RES	RESULTS	
CHARACTER OF FIELD	NaCN	Water	Additional	TREATED	INED INED		DATE TREATED DATE EXAMINED	Dead	Alive	KILL
	lbs.	gal.	gal.	sq.ft.	sq.ft.	6761	6161			percent
	110	Dry	16,000	100	6	Sept. 15	Sept. 19	108	37	74+
	165	Dry	16,000	100	6	Sept. 15	Sept. 19	95	24	+64
	220	Dry	16,000	100	6	Sept. 15	Sept. 19	96	2	+16
Woods—thin weeds	110	16,000	None	100	6	Sept. 16	Sept. 19	85	12	+88
	165	16,000		100	6	Sept. 16	Sept. 19	88	4	95+
	220	16,000		100	6	Sept. 16	Sept. 19	95	3	-16
	C	C heck			6		Sept. 19	0	45	0
	110	Dry		100	6	Sept. 18	Sept. 22	9	20	23+
	165	Dry	16,000	100	6	Sept. 18	Sept. 22	S	10	33+
	220	Dry	16,000	100	6	Sept. 18	Sept. 22	9	-	85+
	110	16,000	None	100	6	Sept. 18	Sept. 22	1	0	100
	165	16,000	None	100	6	Sept. 18	Sept. 22	3	0	100
	220	16,000	None	100	6	Sept. 18	Sept. 22	19	0	100
	C	Check			6		Sept. 22	0	84	0
	164	92669	None	100	6	Oct. 15	Oct. 20	21	19	52+
	563	92669	None	100	6	Oct. 15	Oct. 20	34	22	-19
Commentation London Georgebra	113	92669	None	100	6	Oct. 15	Oct. 20	35	15	70
Campbell's neavy thirdday	57	92669	None	100	6	Oct. 22	Oct. 27	17	9	74+
	57	92669	Watered	100	6	Oct. 22	Oct. 27	10	∞	55+
	85	92669	None	100	6	Oct. 22	Oct. 27	21	11	-99
	82	92669	Watered	100	6	Oct. 22	Oct. 27	23	1	-11
	1133	92669	None	100	6	Oct. 22	Oct. 27	18	4	82-
	$113\frac{1}{2}$	92669	Watered	100	6	Oct. 22	Oct. 27	16	S	494
	170	92669	None	100	6	Oct. 22	Oct. 27	12	2	-98
	1704	926'9	Watered	100	6	Oct. 22		14	0	100
	57	926'9	None	100	6	Oct. 29		13	4	+91
	57	6.976	Watered	100	0	Oct 20		4	0	67 1

	55	926.9	None	100	6	Oct. 29		17	3	85
	85	926'9	Watered	100	6	Oct. 29		3	2	99
1 2 1 2	1131	92669	None	100	6	Oct. 29		15	1	-16
Campbell's neavy timotiny	1131	9,676	Watered	100	6	Oct. 29		6	-	06
	1704	92669	None	100	6	Oct. 29		12	0	100
	1704	926,9	Watered	100	6	Oct. 29		13	-	93-
	750	4,650	Heavy	100	6	Oct. 31	Nov. 4	15	121	55+
			Watered							
	38	4,650	Heavy	100	6	Oct. 31	Nov. 4	6	161	36
West Learner Planeman			Watered							
Woods—neavy bluegrass	458	5,580	Heavy	100	6	Oct. 31	Nov. 4	9	141	30
			Watered							
	57	92669	Heavy	100	6	Oct. 31	Nov. 4	3	21	09
			Watered							
	1			000	,			7	<	9
	2/	1,308	Watered	100	0	Oct. 4	Oct. 8	21.	>	301
Riverton lawn	1132	2,614	Watered	100	3	Oct. 4	Oct. 8	292	0	100
	$164\frac{1}{2}$	3,920	Watered	100	3	Oct. 4	Oct. 8	402	0	100
	453	5,568	Watered	100	4		Nov. 3	263	4	87-
Cinnaminson lawn	57	896'9	Watered	100	4	Oct. 30	Nov. 3	454	16	74-
	38	4,646	Watered	100	4	Oct. 30	Nov. 3	716	12	85+
	57	92669	Watered	100	43	Oct. 16	Nov. 20	416	0	100
Burlington lawn	$113\frac{1}{2}$	3,924	Watered	100	42	Oct. 16	Nov. 20	1197	0	100
	1701	3,924	Watered	100	1	Oct. 16	Nov. 20	268	0	100

1 Live grubs 5 to 6 inches deep.

 $^2$  All Cyclocephala grubs except one which was Lachmosternu.  $^3$  Eighteen Cyclocephala—all dead.

\* Forty Cyclocephala—90 per cent dead.

5 Seventy-six Cyclocephala-85 per cent dead.

7 One hundred and six Cyclocephala and 13 Macrodactylus. <sup>6</sup> Twenty-four Cyclocephala and 17 Macrodactylus.

8 Eighteen Cyclocephala and 8 Macrodactylus.

and where a field of several acres was being treated it has been found most economical to use three tanks, two tractors and three men, one to mix and the other two to drive the tractors. As one tank was emptied the driver returned to the water-supply pipe, there leaving the empty tank to be filled and returning to the field with a full tank. The empty tank was filled by the time the other tank in the field was emptied and thus the cyaniding operations were continuous with no loss of time for tractors or men. By this method 3 tanks can cover 3 acres in a day. Where it is possible to approach the water pipe from both sides one stand-pipe is sufficient but where it is necessary to fill along roadways it is necessary to place two stand-pipes, to prevent blocking the road as illustrated in plate 2, figure 1. By this method and by using granular sodium cyanide (96 to 98 per cent cyanogen) at 165 pounds per acre the cost per acre for material (cyanide  $26\frac{1}{2}$  to  $30\frac{1}{2}$  cents) and labor (\$4.00 to \$5.00 per day) was \$49.00 to \$56.50

Dry cyanide was applied by broadcasting for small plots and with a fertilizer drill for larger plots. The latter method is not entirely satisfactory on account of clogging, especially in moist weather.

The results of a series of experiments given in tables 3 and 4 are worth recording. The tests and examinations were made by men familiar with our methods of applying the insecticide and with methods of making examinations but not otherwise experienced in entomological practices. The experiments are somewhat miscellaneous in nature, as it was impossible to follow up all details on account of pressure of other work and the services of an experienced experimenter were not available.

In obtaining the results, areas 1 by 9 feet were dug at more or less regular intervals in the treated field. An eye hoe was used for this purpose and the loosened soil (pl. 2, fig. 2) was then carefully examined by hand to determine the number of dead and live grubs. Where the plots were small individual square feet instead of square yards were examined.

In general, our observations clearly indicate that the percentages of mortality as given in tables 3 and 4 are low, since the grubs, especially the smaller ones, disintegrated rapidly after death and were easily overlooked. It was found that ground covered with timothy, weeds or similar vegetation permitted better penetration of the insecticide if the crop was closely mowed and consequently a more satisfactory kill was obtained than where the vegetation was tall or matted. Applications of dry cyanide, broadcasted or drilled, and the treated area afterwards watered gave appreciably and uniformly poorer results than where the cyanide was applied in liquid form. Where comparisons were possible we observed that cyanide was more effective against Cyclocephala, Lachnosterna, and Macrodactylus grubs than against Popillia; in some cases the difference was apparently due to greater resistance and in some cases because the Popillia grubs were earlier influenced by approaching cold weather and had penetrated deeper during the latter part of October than had the other grubs.

Little is known of the effect of cyanide treatment on soil. Byers (3) reports no serious injurious or retarding effect on the germination or growth of dasheens where sodium cyanide had been applied, but that small quantities increased the growth and larger treatments retarded growth the first season; others report similarly. In our own experiments it was found that grass might be burned by the cyanide solution but that there was no permanent injurious effect except where the liquid stood in low places for a considerable period of time. Cultivated crops such as corn were appreciably injured by the treatment. We have no definite observations on the permanent effect of cyanide treatment on the soil but we do know, from chemical analyses made by C. S. Cathcart, state chemist of New Jersey, that the cyanide disappears in the course of a week or ten days after treatment or even in a shorter period in case it rained during the interval. J. C. Clark, of the Henry A. Dreer Company, used soil treated with sodium cyanide (1 and 2 ounces per 100 pounds) and sodium cyanide with ammonium sulfate (2 ounces NaCN and 3 ounces (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> per 100 pounds of soil) for several varieties of seedling ferns and found no serious injurious after-effect, except to certain sensitive varieties, particularly the holly fern which died when started in soil previously treated as above. Walter S. Lenk, of the Roessler and Hasslacher Chemical Company, has kindly furnished us with numerous reports of experiments and observations made by F. A. Kaufmann and R. N. Sargent, which give further light in the use and value of sodium cyanide as a soil insecticide. Their results indicate the value of a combination of granular sodium cyanide and ammonium sulfate (400 pounds NaCN and 500 to 600 pounds (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> per acre) the two being added to the soil successively and thoroughly mixed. The addition of ammonium sulfate accelerates the decomposition of cyanide and not only gives a prompt reaction but is at the same time a fertilizer of some value. They found that soil thus treated could be safely planted with most crops one to two weeks after treatment. We have had no personal experience with sodium cyanide in combination with ammonium sulfate. Before cyanide can be recommended for use in sterilizing greenhouse soil many more experiments will be necessary to determine the chemical effect on soil treated and the effect on different kinds of greenhouse plants when such soil is used for potting and seed-beds.

It is evident for the foregoing remarks that while many isolated experiments have been conducted to determine the possible use of sodium cyanide as a soil insecticide, the whole study, which is a most important one, lacks continuity and until a consistent and continuous program of investigation is vigorously inaugurated by some institution, preferably the United States Department of Agriculture, we cannot look for other than fragmentary results and temporary conclusions.

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## PLATE 1

- Fig. 1. Cyaniding tank, illustrating improper application resulting when a few large holes are used in the distributor pipe.
- Fig. 2. Uniform distribution and better penetration is secured when the holes in the distributor pipes of the cyaniding outfit are smaller and numerous.



Fig. 1



Fig. 2

# PLATE 2

Fig. 1. Filling station for large-scale cyaniding operations.

Fig. 2. Examining soil to determine effect of soil insecticide treatments.

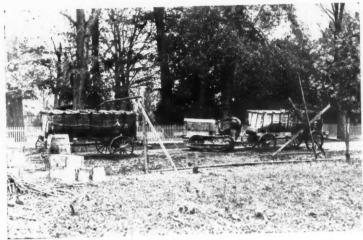


Fig. 1



Fig. 2



